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ARTICLE

Applications of Catalysis in Hydroboration of Imines, Nitriles, and Carbodiimides

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The catalytic hydroboration of imines, nitriles, and carbodiimides is a powerful method of preparing amines which are key synthetic intermediates in the synthesis of many value-added products. Imine hydroboration has perennially featured in notable reports while nitrile and carbodiimide hydroboration have gained attention recently. Initial developments in catalytic hydroboration of imines and nitriles employed precious metals and typically required harsh reaction conditions. More recent advances have shifted toward the use of base metal and main group element catalysis and milder reaction conditions. In this survey, we review metal and nonmetal catalyzed hydroboration of these unsaturated organic molecules and group them into three distinct categories: precious metals, base metals, and main group catalysts. The TON and TOF of imine hydroboration catalysts are reported and summarized with a brief overview of recent advances in the field. Mechanistic and kinetic studies of some of these protocols are also presented.

1. Introduction

First reported by H. C. Brown in 1956, hydroboration is the addition of a boron-hydrogen bond across an unsaturated moiety.[1] In these reactions, the boron containing group acts as a functional handle to form a new carbon-carbon bond or to introduce functional groups such as alcohols, amides, amines, or halogens.[2] Usually, the reaction proceeds without the addition of a catalyst and the borane reagent, such as diborane (B_2H_6) or a borane adduct (BH_3·THF), reacts rapidly at room temperature to afford an anti-Markovnikov organoborane. Nonetheless, when using pinacolborane (HBpin) and catecholborane (HBcat), the boron is bonded to a heteroatom which results in increased electron density at the boron center.[3] As a consequence, the Lewis acidity of the boron center decreases, thus requiring increased temperatures or the addition of some catalyst or co-reagent for hydroboration to proceed efficiently.[4, 5]

The first catalytic hydroboration process was disclosed in a report by Kono and Ito in 1975. They reported that Wilkinson's catalyst [$Rh(PPh_3)_3Cl$] can undergo oxidative addition with catecholborane (HBcat).[6] A decade later, Manning and Nöth demonstrated that Wilkinson's catalyst along with HBcat catalyzed hydroboration of a C=C bond selectively in the presence of a keto group.[7]

To date, catalysts ranging from main group elements [8-13] and transition metals [14-20] have been extensively developed for the hydroboration of unsaturated organic molecules.[21-26] These continue to be of interest in chemical syntheses of complex molecules as well as the production of commodity and agrochemicals. Amongst unsaturated species, nitrogen containing compounds such as imines, nitriles, carbodiimides etc. have garnered considerable attention in the application of hydroboration processes. This is due to primary and secondary amines being extensively present in nature. They are important compounds in chemistry and biology with versatile application in the synthesis of agrochemicals[27], drug molecules [28, 29] and polymer materials.[30] Furthermore, borylated amine products which form in the hydroboration of nitrogenous compounds can act as an excellent synthetic surrogates. Traditional protocols for such transformations, for example, in the production of amine products employ metal hydrides [31-33] and pressurized hydrogen gas as hydrogen source [34-42] are well-exploited. Nevertheless, these methods suffer from poor selectivity and limited functional group tolerance as well as the deleterious formation of inorganic byproducts, and safety concerns. Hydroboration offers an efficient pathway into the preparation of amines through: 1) chemoselective reduction and, 2) modest reaction conditions and energy requirements.[43]

The milestone discovery of imine hydroboration, which was first introduced by the Westcott group[44], led to the development of a plethora of transition metal and main group element complexes as the catalyst ranging from precious [45-48], to rare earth [49, 50] and even base metal complexes.[51, 52] A β-diketiminato magnesium complex was reported in 2013 as a main group element pre-catalyst in the hydroboration of imines.[53] Following on from such pioneering works, other metal and non-metal main group complexes were developed in related hydroboration transformations.[53-65] Catalyst free imine hydroboration was also recently introduced by the Rit group.[66]

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Nitrile hydroboration, operating through the formation of an imine intermediate,[49] was only introduced less than a decade ago by Nikonov and co-workers who employed an imido-hydrido complex of Mo (IV).[67] Significant progress has been made in the development of nitrile hydroboration using main group elements [31, 63, 68-72] and transition metals (d- and f- blocks) in recent years.[47, 73-76] One report in 2019 exploited a thorium amide complex in nitrile hydroboration by Eisen and co-workers featuring a broad substrate scope and high TOF (500 h^{-1}). This was an unusual example of actinide catalysis and takes advantage of the low cost of thorium and the stability of the Th(IV) oxidation state.[49] There are also reports involving the further transformation of N-boryl amines in the coupling reactions to form N-arylation or N-acylation products[74, 76, 77].

In contrast to the advances in both nitrile and imine hydroboration, analogous heteroallene (E=C=E´: E, E´=RN, RN; RN, O) hydroboration chemistry, such as carbodiimides, are not well characterized.[78, 79] In 1994, the single and double hydroboration of carbodiimide was demonstrated in the presence of 9-borabicyclo[3.3.1]-nonane (9-BBN) without the need for a catalyst. Amidinate and bis(boryl)aminal products were obtained, albeit under forcing thermal conditions (160 °C).[80] Almost three decades later, there remains only a handful of reports of carbodiimide hydroboration.[81, 82 62, 63]

Numerous catalysts have been reported to effect the hydroboration of imines, nitriles and carbodiimides. Notably, the current state-of-the-art still relies mainly upon precious metal elements. However, the limited availability, high and volatile cost and toxicity of precious metal catalysts has shifted recent focus towards the development of inexpensive and environmentally benign first-row transition metal complexes as alternatives.[83] This review outlines the advances *and* challenges in this field as well as new avenues to efficiently catalyze hydroboration of imines, nitriles and carbodiimides.

2. Hydroboration of imines

2.1. Precious metal catalyzed hydroboration of imines

Transition metals such as Pt, Pd, Ru, Rh and Ir (known as precious metals) have been the most active and catalytically effective metal complexes in transformations of unsaturated organic molecules for decades.[84, 85] This is in large part owing to their capacity to accommodate $2e^-$ redox processes.[86] As such, they have found extensive application in both academia and industry in transformations such as hydroboration[87], hydrosilylation[88, 89], amination[90, 91] amongst others.

The first transition metal-catalyzed imine hydroboration was reported by Baker and Westcott in 1995.[44] A wide variety of metal complexes of Cu, Ag, and Au were studied. $[AuCl(L)]_n$ complexes (1 mol %) were found to be the most catalytically efficient and afforded N-borylamine products in the presence of HBcat (**Figure 1**). The hydroboration reaction was monitored by ^1H NMR over several half-lives and the results were normalized to give an estimate of the relative rates. $[AuCl(\mu\text{-DPPF})]_n$ exhibited the highest relative rate in hydroboration of $PhCH_2N{=}CHPh$ in THF-d_8.[44]

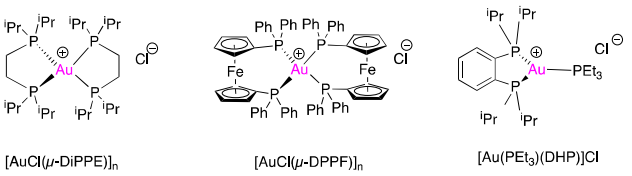
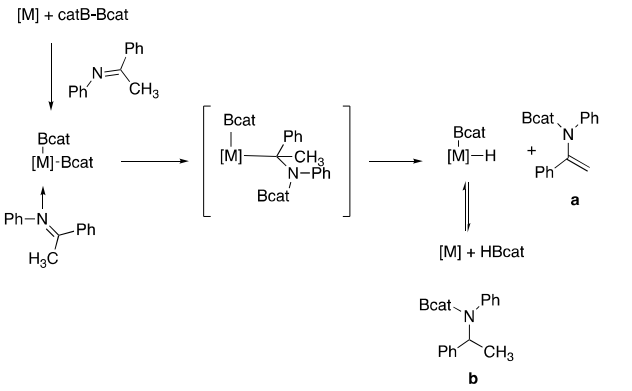


Figure 1. Au(I) complexes used in hydroboration of imines.[44]

Subsequent work from the same research group in 1998 reported that 2 mol % $RhCl(PPh_3)_3$ could be employed at room temperature (25 °C) in the hydroboration of $PhN{=}C(CH_3)Ph$ in the presence of $B_2cat´_2$ (cat´ = 4-But-1,2-$O_2C_6H_3$).[92] The reaction produced equal amounts of N-borylenamine (**Scheme 1a**) and N-borylamine (**Scheme 1b**) products as determined by NMR spectroscopy. The reaction was proposed to follow the pathway shown below (**Scheme 1**): 1) Oxidative addition of the diboron species to the metal center; 2) Coordination of the imine with subsequent regioselective insertion



Scheme 1. Rh catalyzed hydroboration of ketimine.[92]

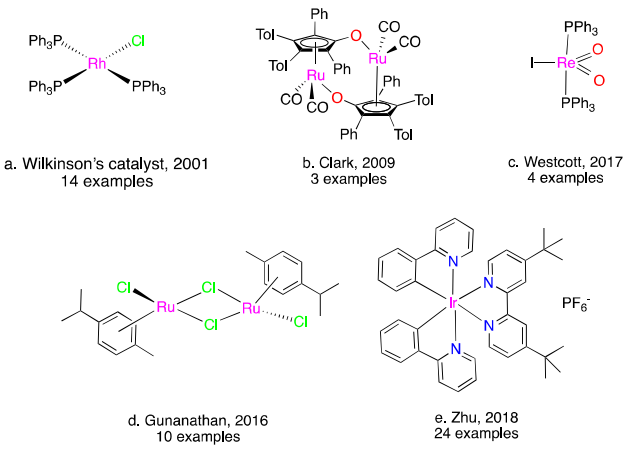


Figure 2. Precious metal catalysts in imine hydroboration.

into the M–B bond; 3) β-H elimination to generate the borylated amine.[92] Baker and Westcott also introduced the first application of Rh-catalyzed (Wilkinson's catalyst) hydroboration of an imine using HBpin in 2001.[45]

Subsequently in 2009, a boron-substituted analogue of the Shvo hydrogenation catalyst was introduced by Clark and coworkers in the hydroboration of aldehydes, ketones, and imines (**Figure 2b**). This is an example of a ligand-metal bifunctional catalyst which forms the boron-substituted catalyst in situ upon the addition of HBpin to the ruthenium dimer complex (**Figure 3**). Clark's report only elaborates a small number of imine substrates which undergo hydroboration (**Table 1**). Hydroboration occurs under 2-4 mol % catalyst loading at 70 °C in 17-120 h. The presence of electron-withdrawing groups within the substrate was found to increase the reaction rate.[48]

A more comprehensive report applying Ru for metal catalyzed imine hydroboration emerged in 2016 from the Gunanathan group (**Figure 2d**), in which a commercially available $[Ru(p\text{-cymene})Cl_2]_2$ precatalyst at low catalyst loadings (0.1 mol %) was employed. This readily available complex catalyzed imine hydroboration via a proposed monohydrido-bridged intermediate $[\{(\eta^6\text{-p-cymene})RuCl\}_2(\mu\text{-H-}\mu\text{-Cl})]$ to form boronate amines. The reaction can be efficiently carried out at 60 °C in as little as 15 h with a much wider substrate scope compared to earlier reports employing Ru catalysts (10 examples). The formed boronate amines are conveniently hydrolyzed using silica gel in methanol for 6 h at 50 °C. The resulting secondary amines were isolated using column chromatography providing good yields (83-92 %, **Scheme 2**).[47]

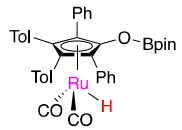
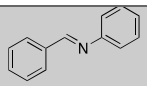
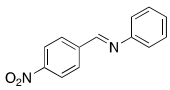
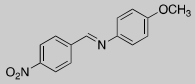
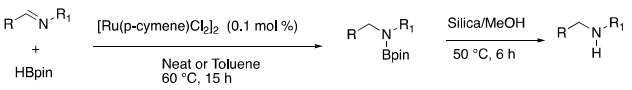


Figure 3. Ruthenium catalytic active species.[48]

Table 1. Catalytic hydroboration of imines[48]

Entry	Substrate	Time (h)	Yield[a] (%)
1[b]		120	82
2		22	86
3		17	74

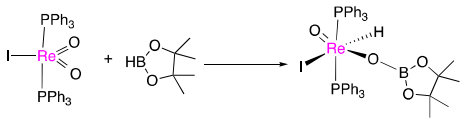
[a]Isolated yield of amines. [b]4 mol % Ru catalyst is used.



Scheme 2. Hydroboration of imine catalyzed by $[Ru(p\text{-cymene})Cl_2]_2$ and the conversion of amine boronates to secondary amine.[47]

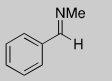
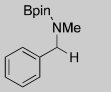
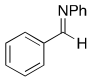
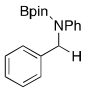
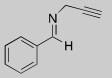
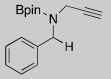
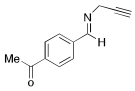
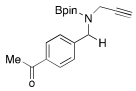
In 2017, a series of commercially available Re complexes were applied in several catalytic reactions by the Westcott group. The high-oxidation state complex of $[(PPh_3)_2Re(O)_2I]$ was found to be an efficient precatalyst in imine hydroboration; however, the scope of substrate studied was limited (4 examples). N-benzylidenemethanamine was found to be reduced smoothly using 5 mol % Re catalyst, 1.1 eq HBpin at 80 °C within 2 h. However, aldimines derived from aromatic primary amines were found to be quite sluggish in this reaction (**Table 2**). Surprisingly, (E)-N-benzylideneprop-2-yn-1-amine proceeded in a chemoselective fashion which resulted in hydroboration exclusively at the C=N, while the alkyne group remained intact. It is proposed that the mechanism of this reaction is similar to that outlined by Fernandes and co-workers, through 1,2-addition across Re=O pi bond to generate a reactive rhenium hydride species along with a [Re]-OBpin group (**Scheme 3**).[93] This is the only Re-catalyzed imine hydroboration reported to date.[94]

Remarkably, a photocatalytic *inverse hydroboration* of imine was introduced in 2018 by Zhu and coworkers to produce α-amino organoborons.[46] These α-amino organoborons are potentially quite versatile building blocks in the synthesis of protease inhibitors and compounds for medicinal chemistry. In this work, they utilized N-heterocyclic (NHC) carbene boranes in the catalytic system along with the $*Ir\text{-}(ppy)_2(dtbbpy)PF_6$ complex (**Figure 2e**) in the presence of phenylmethanethiol and NaH as the inorganic base under the irradiation of 33 W CFL at room temperature. The photoexcited $*Ir\text{-}(ppy)_2(dtbbpy)PF_6$ complex readily accepts one electron from thiol ($C_6H_5CH_2SH$) to form thiyl radical which can then reactively generate NHC-boryl radicals. This method is different from conventional strategies using toxic radical initiators to form active radical species.[46] Two possible pathways were proposed for inverse imine hydroboration which is shown in **Scheme 5**. Intermediate a (**Scheme 5**) was trapped by 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO).

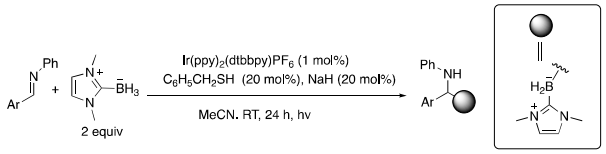


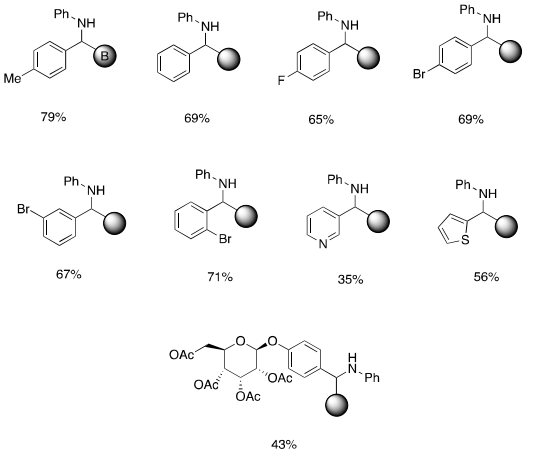
Scheme 3. Addition of HBpin to $[(PPh_3)_2Re(O)_2I]$.[93]

Table 2. Rhenium-catalyzed hydroboration of aldimines[94]

Entry	Substrate	Product	Yield
1			100
2			25
3			100
4			100

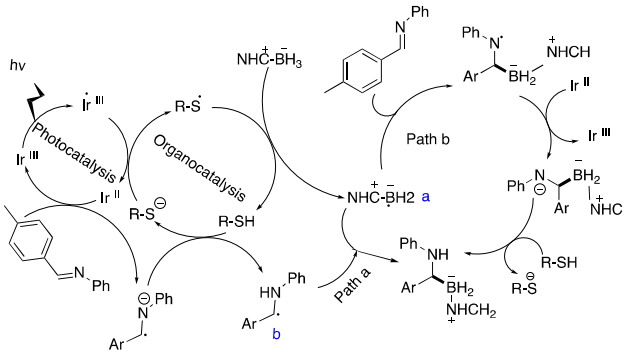
Reactions were carried out in a sealed J. Young tube. 5 mol % $[(PPh_3)_2Re(O)_2I]$ with pinacolborane. Conversion ascertained using 1H NMR spectroscopy averaged over three runs.





Scheme 4. Selective catalytic inverse hydroboration of imine with N-heterocyclic carbene (NHC) boranes.[46]

Path (a) proposed a single electron transfer (SET) reduction of the imine with strongly reductive Ir^{II} followed by radical-radical C-B cross-coupling of the NHC-boryl radical with the α-amino-benzyl radical. Path (b) suggested that NHC-boryl radical addition to the imine occurs first, with subsequent SET reduction of the nitrogen-centered radical. Both experimental and density functional theory (DFT)



Scheme 5. Mechanistic hypothesis of Iridium catalyzed inverse imine hydroboration.[46]

studies were employed to study the mechanism and revealed that a key factor in the reaction is the thiol organocatalyst; it facilitates the formation of boryl radical and suppresses the ionic reduction pathway.[46] Both radical intermediates (Scheme 5- a & b) were detected in the reaction process. However, the radical chain pathway (path a) is considered a minor contributor as the quantum yield of the model reaction was determined as 0.35.[46]

2.2. Base metal catalyzed hydroboration of imines

Although catalysis is a fundamental pillar of green chemistry, the use of sustainable and less toxic reagents and catalysts represents an additional improvement to this strategy.[95] The scarcity and toxicity of precious metals has increased the demand for inexpensive and more environmentally benign surrogates. Base metal catalysts, like first row transition metal complexes, are generally less expensive and have much lower toxicity.[3]

The first report of a base metal catalyzed imine hydroboration was disclosed in 2016. Gordon group reported Ni(bpy)(cod) (**Figure 4a**) to be an effective catalyst in imine hydroboration.[51] The metal center in

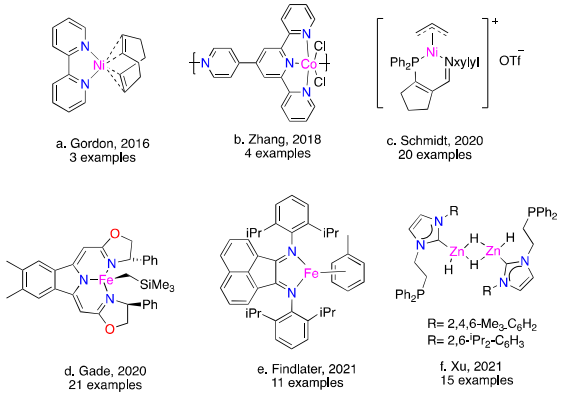


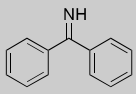
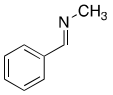
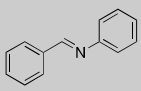
Figure 4. Base metal catalysts in imine hydroboration.

this example is supported by a redox-active bipyridine ligand and this complex has been deployed in a range of both catalytic and stoichiometric transformations: ring-opening of aziridines[96], α-amino acid N-carboxy anhydrides[97], coupling of CO with 1,2-diphenylacetylene[98] and, the dimerization of 1,4-substituted allenes[99] amongst others. It was proposed that the addition of pinacolborane as an external reductant in these reactions helped to facilitate the release of the reduced substrate from the nickel center and regenerate the catalytically relevant [Ni(bpy)] moiety. To illustrate the redox non-innocent nature of the ligand, a single-crystal X-ray diffraction experiment revealed a molecular structure consistent with a $Ni^{I}(bpy^{\cdot-})$ fragment with a nickel center in a pseudo-tetrahedral environment. This catalyst can reduce aryl-substituted imines in excellent yields (up to 96 %) at 25 °C. The reaction conditions are mild with low catalyst loading (0.3 mol %) and the reaction is complete within 2.5 h; however, the scope of substrate examined was limited to only three examples (**Table 3**).[51]

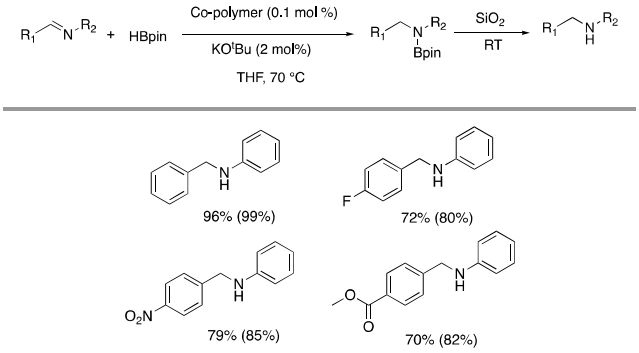
A heterogeneous cobalt(II) coordination polymer precatalyst (**Figure 4b**) was developed by the Zhang group in 2018.[52] This precatalyst is effective in imine hydroboration in the absence of any air- or moisture-sensitive organometallic reagents. Several aromatic imines with fluoro-, nitro- and ester-groups were studied as substrates. In all cases, the corresponding amine products could be obtained in good to excellent yield (up to 96 %). The reaction conditions are presented as described in **Scheme 6** with 0.1 mol % cobalt coordination polymer as catalyst along with 2 mol % KO^{t}Bu in imine hydroboration at 70 °C in THF. This Co^{II} coordination polymer catalytic system has the benefit of being air stable, highly efficient, and reusable.[52]

In 2020, a cationic [(iminophosphine)nickel(allyl)]$^{+}$ complex (**Figure 4c**) was reported to effect catalytic imine hydroboration by Schmidt and coworkers. With loadings as low as 5 mol %, smooth conversion of N-allylimine substrates to their corresponding amine products was observed. Yields as high as 92 % were obtained in the presence of 1.2 eq. HBpin at room temperature. Slightly sluggish reaction rates were observed in substrates with electron withdrawing groups.[100]

Table 3. Catalytic hydroboration of imines with Ni(bpy)(cod)[51]

Entry	Substrate	Catalyst (mol %)	Time (h)	Yield[a] (%)
1		0.3	2.5	83
2		0.3	2.5	89
3		0.3	2.5	96

[a]General condition: C_6D_6 as solvent, room temperature. 1H NMR yields using tert-butylbenzene as an internal standard.



Scheme 6. Cobalt (II) coordination polymer catalyzed hydroboration of imine[52]. Reaction conditions: Imines (1.0 mmol), HBpin (1.1 mmol), cobalt CP (0.1 mol %), KO^{t}Bu (2 mol %), and THF (1 mL), 70 °C, 16 h, N_2. Yields of isolated products of amines with GC conversion of imines are shown in parentheses.

In the same year, the Gade group reported an iron alkyl precatalyst (**Figure 4d**) in the enantioselective hydroboration of N-alkyl imines. A chiral bis(oxazolinylmethylidene)isoindoline pincer ligand was deployed in the asymmetric reduction of acyclic N-alkyl imines. Low catalyst loading of 0.5-3 mol % is used in the presence of HBpin at -40 °C and a wide range of substrates studied afforded excellent yields (31-99%) with up to >99 % ee.[101]

At the beginning of 2021, the Findlater group reported the use of ^{dpp}BIANFe(Tol) as precatalyst in the rapid hydroboration of aldimines and ketimines to afford the corresponding secondary amines after hydrolysis through silica and hexanes. Low catalyst loadings (1 mol %) are employed in the presence of HBpin and NaO^{t}Bu at 70°C. In general, yields ranged from 46-99%, and most notably, the reaction was also effective in substrates featuring steric encumbrance with good to moderate yields observed (43-63%). Products can be readily isolated as ammonium salts. The synthetic utility of the reaction was demonstrated using gram scale reactions in which 90% isolated yield was obtained in a gram-scale reaction of N-benzylideneaniline.[102] The mechanism of the reaction was probed using kinetic, stoichiometric, and temperature-dependent rate experiments which suggest the formation of metal hydride species in the reaction mechanism. Subsequently, formation of an iron(boryl)(amine) was proposed to occur upon insertion of the C=N bond into the iron-hydride species.[102]

The first example of a zinc-catalyzed imine hydroboration was reported in 2021 by the Xu group.[103] In this example, a zinc dihydride complex stabilized by N-heterocyclic carbene ligands was shown to be highly efficient in catalytic hydroboration of nitriles and imines under low catalyst loading (0.5 mol %) and neat (solvent-free) conditions at room temperature. A wide scope of aldimines underwent rapid hydroboration. Most of the substrates reduced within 10-40 min with 82-92 % isolated yields. However, aliphatic and sterically hindered substrates required longer reaction time (6-16h) with 84-92 % isolated yields.[103]

2.3. Rare earth metal catalyzed hydroboration of imines

Despite the widespread application of transition metal complexes as catalysts in imine hydroboration chemistry, rare earth metals (the f-element lanthanides and actinides) have not been as widely studied

(**Table 4**). A boratabenzene metal complex capable of reducing unsaturated organic molecules was first reported in 2011 (**Figure 5a**).

The Xia group reported 1-H-boratabenzene complex of Y (Yttrium) in the hydroboration of alkenes, imines, and carbodiimides as a metal ion dependent hydroboration. Boratabenzene is isoelectronic with the cyclopentadienide anion (Cp^*), and the catalytic behavior of boratabenzene metal complexes are greatly influenced by the boron substituent, due to the higher reactivity of the B-H bond as compared to the C-H bond on the ubiquitous Cp ligand (**Figure 6**). The yttrium complex $[C_5H_5BH]_2YCl$ was prepared *via* the metathesis reaction between $[C_5H_5BH]Li$ and anhydrous YCl_3 in toluene. The hydroboration of benzylidene-n-propylamine, using $[C_5H_5BH]_2YCl$, resulted in the amino-substituted boratabenzene complex $[C_5H_5BN(^nPr)CH_2Ph]_2YCl$ in excellent yield (94%).[104]

In 2018, the Wang group reported a series of amidate-functionalized N-heterocyclic carbene (NHC) rare-earth metal (Er, Y, Gd, Dy) amido complexes in the hydroboration of imines and nitriles.[50] These complexes were synthesized via reaction between ligand precursor, (L= 1-(C_6H_5C=ONCH$_2$CH$_2$)-3-(CH_3)$_3C_6H_2$(N(CH)$_2$NC)), $RECl_3$ (RE = Er , Y , Dy, Gd) and $KN(SiMe_3)_2$ (KHMDS) in a one-pot fashion as depicted in **Scheme 7**. All complexes were crystallized to afford pure products from tetrahydrofuran (THF)/ n-hexane and characterized by IR spectroscopy and elemental analysis.
The complexes of Er and Gd turned out to be the most effective catalysts with high product yields of 96% and 95 % respectively, in the hydroboration of benzylideneaniline (2 mol % catalyst loading).[50] The optimized reaction conditions were established to be 2 mol % catalyst, 1.5 eq of HBpin, 0.5 ml toluene at a reaction temperature of 110 °C for 6 h. Various imine substrates were subjected to these hydroboration conditions employing the Er complex as the catalyst under study. The reaction afforded the desired secondary amines in excellent yields (50-99 %) after work-up with column chromatography (methanol/silica gel). Several different functional groups including halogens, ethers and hydroxyl groups exhibited little effect on the progress of the reaction and were well tolerated. However, the presence of the strongly electron-withdrawing $-NO_2$ group resulted in a decreased yield of 50%, and thus, it was proposed that the strongly electron-withdrawing nature of this group helped to disfavor the coordination of the imine to the metal center. Additionally, the chelation of the oxygen atoms of the nitro group to the metal center of the catalyst is also a possibility that would reduce the catalyst efficiency.[50] A plausible reaction mechanism was proposed as depicted in **Scheme 8**. The proposed mechanism postulated the formation of a rare-earth metal hydride species via σ-bond metathesis as a key step. Subsequently, imine C=N insertion into the Er-H bond is followed by the reaction with another HBpin molecule to release the product and regenerate the active metal hydride species.[50]

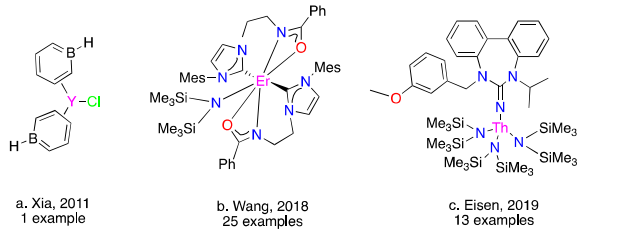


Figure 5. Rare earth metal catalysts in imine hydroboration.

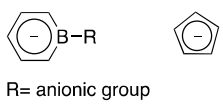
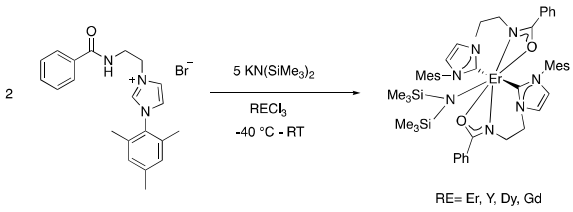


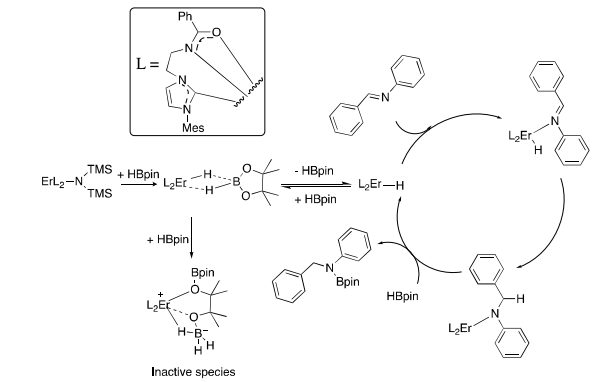
Figure 6. 6π-Electron aromatic anions: Boratabenzene and Cyclopentadienyl.[104]

Subsequently, the Eisen group developed an N-heterocyclic iminato thorium complex (**Figure 5c**) capable of catalyzing the hydroboration of aldimines in 2019. The Th(IV) precatalyst was synthesized by the protonolysis of a seven-membered N-heterocyclic iminato ligand and a metallacyclic thorium amide complex $[(Me_3Si)_2N]_2Th[\kappa_2–(N,C)–CH_2Si(CH_3)_2N(SiMe_3)]$. Hydroboration of N,1-diphenylmethanimine yielded 95% hydroborated amine product in the presence of 1 mol % Th catalyst upon heating to 80 °C after 24h. A wide range of aldimines bearing electron-donating, withdrawing, neutral and aliphatic groups were studied with excellent yields (80-100 %) to form hydroborated secondary amines.49 However, this catalytic system was incapable of the hydroboration of ketimines.[49] Stoichiometric reactivity studies, kinetic and temperature dependence measurements were performed in order to gain insight into the mechanism of the reaction. An analysis of the reaction kinetics revealed a first-order dependence on the catalyst concentration, HBpin, and no dependence on imine concentration (eq 1).

$$eq\ 1. \quad \frac{\delta p}{\delta t} = k_{obs} \times [Th]^1\,[HBpin]^1][PhC = NPh]^0$$



Scheme 7. Synthesis of rare earth metal complexes.[50]

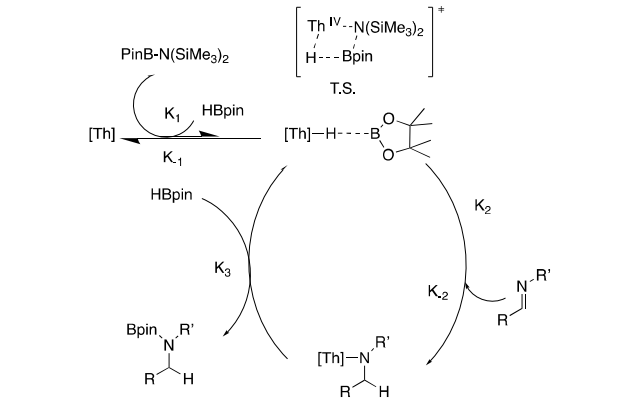


Scheme 8. Proposed reaction mechanism for imine hydroboration with amidate-functionalized N-heterocyclic carbene (NHC) Er complex.[50]

Table 4. Transition metal catalyzed hydroboration of imines; Comparison of reaction condition

Catalyst	Catalyst mol %	Solvent	Temp(°C)/ Time (h)	TON	TOF (h^{-1})	Ref
Ru 2016	0.1	Toluene	60 / 15	990	66	47
Ru 2009	2	Toluene	70 / 17-120	41	< 1	48
Ir	1	CH_3CN	RT / 24	73	3	46
Re	5	C_6D_6	80 / 2	20	10	94
Ni(bpy)(cod)	0.3	C_6D_6	RT / 2.5	200	80	51
Co	0.1	THF	70 / 16	990	62	52
Th	1	C_6D_6	80 / 12-24	100	8.3	49
Y	50	Toluene	75 / 48	1.87	<1	104
Er	2	Toluene	110 / 6	47	< 8	50
Fe (Findlater)	1	Toluene	70 / 0.5	99	198	102
Fe (Gade)	0.5-3	Toluene	-40-RT/14-56	66	4.7	101
Zn	0.5	-	RT/ 15 min	100	400	103

The activation parameters were calculated from Eyring and Arrhenius plots and $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and E_a values of −36.46 (0.8) e.u., 13.42 (1.06) kcal/mol, and 14.05 (0.77) kcal/mol were obtained, respectively.[49] A highly organized four-centered transition state with concerted bond-cleavage and bond-formation can be inferred from the $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values. One plausible hydroboration mechanism was proposed in which the reaction initiates via σ-bond metathesis between the Th-N($SiMe_3$)$_2$ and HBpin. Subsequently, imine C=N insertion followed by the concerted addition of HBpin via Th-N/HBpin σ-bond metathesis to afford amine product and regenerate the catalytically active species (**Scheme 9**). Unfortunately, no hydride signal (Th-H) or deuteride were detected by NMR spectroscopy which would indicate a rapid exchange equilibrium between the hydride at the metal and at the HBpin.[49]



Scheme 9. Proposed mechanism of Th-catalyzed imine hydroboration.[49]

2.4. Main group element catalyzed hydroboration of imines

Catalysis employing main group elements has been widely studied in the context of hydroboration (**Table 5**). In 2012, Crudden group introduced a Lewis acid-base adduct of DABCO·B(C_6F_5)$_3$ and Ph_3C^+/DABCO (DABCO =1,4-diazabicyclo[2.2.2]octane) in hydroboration of aldimines and ketimines. The reaction between DABCO·B(C_6F_5) or Ph_3C^+/DABCO with HBpin result in three-coordinate boronium ions in situ which can catalyze imine substrates (**Scheme 10a**). Relatively broad substrate scope of aldimines and ketimines (13 examples) were studied with isolated yields of 70-96%. The reaction mechanism proposed to begin with the transfer of a borenium ion from catalyst to imine. The resulting boron-activated iminium ion is then reduced by HBpin which is assisted by Lewis base DABCO according to the low temperature NMR studies (**Scheme 10b**).[105]

Later in 2013, the Hill group investigated the catalytic potential of alkaline earth metal complexes of β-diketiminato magnesium alkyl [LMgnBu] (L = CH[CMe(NDipp)]2 Dipp = 2,6-diisopropylphenyl).53 This Mg complex was previously reported to be an efficient catalyst in hydroboration of aldehydes[106], ketones[106] and pyridines[107]. This complex was also demonstrated to be highly effective precatalyst in imine hydroboration.[53] The reduction of imines proceeded smoothly in the presence of HBpin under mild reaction conditions of 5-10 mol % catalyst loading at 25-70 °C.[53] Imines with primary N-alkyl substituents, such as benzyl, n-butyl, 2-methoxyethyl underwent facile hydroboration under mild reaction conditions. However, the

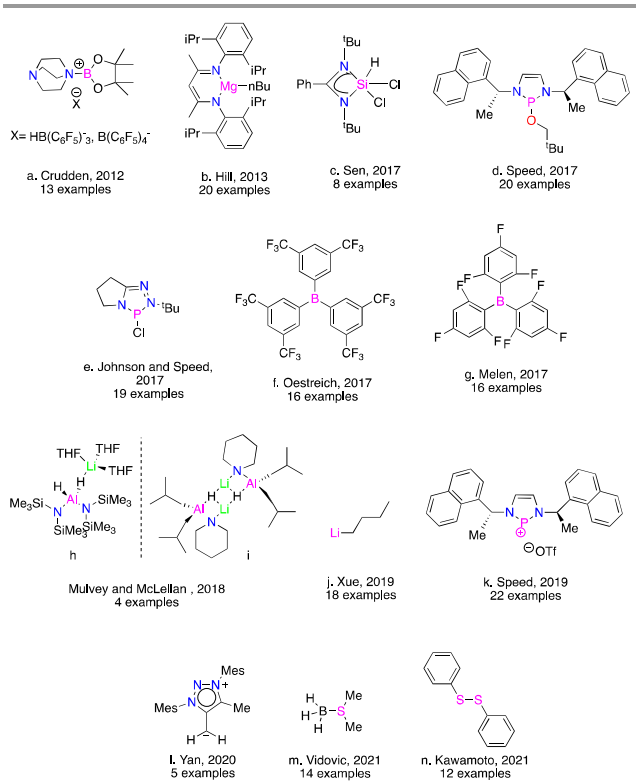
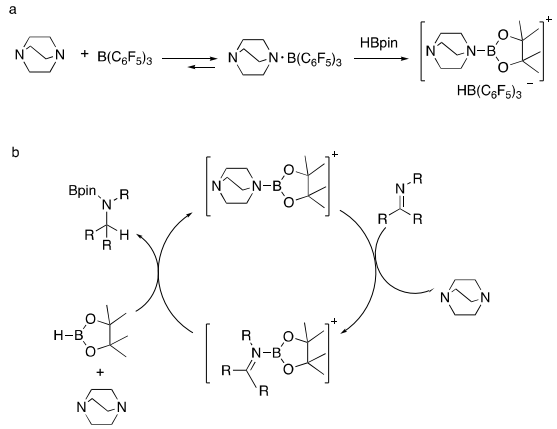


Figure 7. Main group element catalysis in imine hydroboration.



Scheme 10. a Generation of borenium ion in situ. b Mechanism of borenium ion-catalyzed imine reduction.[105]

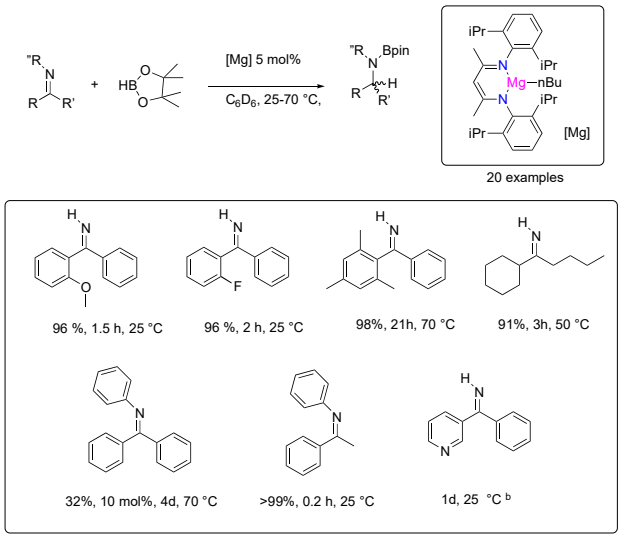
reaction was sluggish for the reduction of substrates bearing secondary (cyclohexyl) or tertiary (tert-butyl) alkyl substituents (1-3 days). The slow rate of reaction is compounded by competing catalyst decomposition over the reaction time period.[53] Interestingly, hydroboration of the pyridine-substituted substrate 3-(PhCH=N)C_5H_4N underwent exclusive hydroboration at the exocyclic imine residue at 50 °C. Selected hydroboration examples of alkyl- and aryl-substituted imines are presented in Scheme 11.[53] Both electron-donating donating and electron-withdrawing substituents in the ortho-position were found to decrease the reaction rate. Ketimines derived from both aryl and alkyl ketones were also underwent successful reduction under increased temperature or catalyst loading.

Careful analysis of stoichiometric studies revealed the formation of (^{n}Bu)Bpin) and [{LMgH}$_2$] as identified by ^{1}H NMR spectroscopy.[53] This is in equilibrium with a magnesium borohydride complex of the [H(^{n}Bu)Bpin]$^-$ ion (**Scheme 12**). Subsequent reaction with one equivalent of PhCH=NPh instantaneously afforded a bright-orange solution which faded over a period of three hours at room temperature. The ^{1}H NMR spectrum of the resulting colorless solution showed complete disappearance of the aldimine and MgH singlets and the formation of an amido complex. Addition of another equivalent of HBpin to this solution at room temperature led to the formation of the hydroborated product $PhCH_2N(Bpin)Ph$.[53]

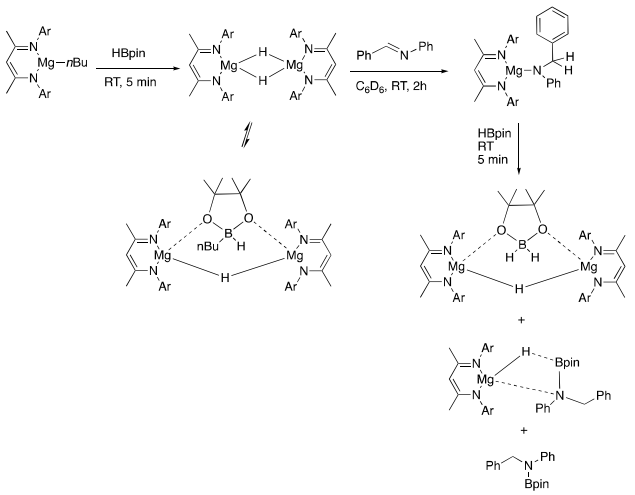
Kinetic studies reveal the reaction to be second order in [imine] and zero order in [HBpin]. In parallel room-temperature experiments using the same catalyst/imine stock solution and 10 equivalents of HBpin, the reaction rate is decreased considerably due to the strong inhibition exhibited by HBpin via coordination to the magnesium center. According to stoichiometric imine insertion and HBpin σ-bond metathesis, the rate law of the reaction is reported as below[53]:

$$\text{rate} = -\mathrm{k}\frac{[\text{cat}][\text{imine}]^2}{\mathrm{k}_{\text{inhib}}[\text{HBpin}]_0} = -k'\frac{[\text{cat}][\text{imine}]^2}{[\text{HBpin}]_0}$$

Main group catalyzed imine hydroboration was extensively studied in 2017 by the Sen group. The catalytic activity of a benzamidinato silane complex, [PhC(N^{t}Bu)$_2$SiHCl$_2$] (**Figure 7c**) was investigated. This silicon (IV) based catalyst can be easily synthesized via a single step in high yield.[108] Electron-donating, -withdrawing and electronically neutral aldimine substrates underwent efficient



Scheme 11. Scope of the magnesium-catalyzed hydroboration for a variety of alkyl- and aryl-substituted imines[53]. [a]NMR yield calculated by integration versus an internal standard of tetrakis(tri-methylsilyl)silane [b]100 % pyridine hydroboration. A complex mixture of 1,2- and 1,4-dihydropyridine and partial imine hydroboration products formed.



Scheme 12. Stoichiometric step-by-step hydroboration of PhCH=NPh by complex [Mg].[53]

hydroboration under 1 mol % catalyst loading in the presence of HBpin at 65 °C. Corresponding secondary amine products were obtained after treating with silica/ methanol at 65 °C. The mechanism is proposed to occur via σ-bond metathesis at the silicon center, followed by the formation of a four-membered transition state and addition of an Si-H bond to the C=N bond (**Scheme 13**). The mechanism was supported by DFT calculations. The energy barrier was calculated to be 40.8 kcal/mol for the bond making and breaking between the Si–N and B– H bond. This high energy barrier explains why the reaction requires elevated temperatures to proceed (65 °C).[109]

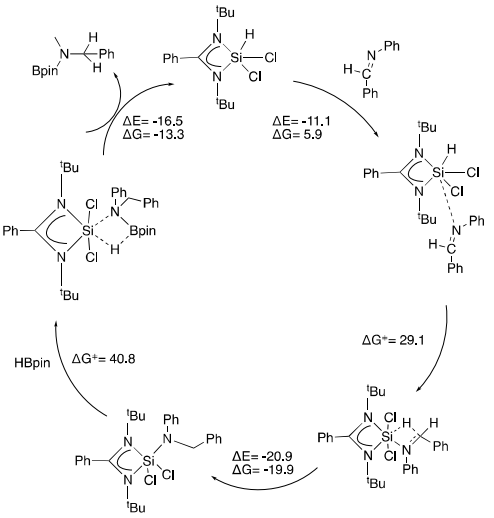
A later study in 2017 reported by Speed and coworkers employed a chiral diazaphospholene catalyst in asymmetric imine hydroboration. Synthesis of this chiral catalyst is relatively straightforward; a three-step process from the commercially available 1-(1-naphthyl)ethylamine through reductive cyclization with PBr_3 in the presence of cyclohexene to give the bromide diazaphospholene. No chromatographic purification is required (**Scheme 14**).[55] Several diazaphospholene (DAP) catalysts with various chiral groups were then explored in the hydroboration of imine substrates as the precursor to therapeutic entrasagiline. A diazaphospholene catalyst bearing larger and more rigid 1-naphthyl aromatic side chains demonstrated the highest enantioselectivity for the hydroboration of alkyl imines _enantiomer ratios of up to 88:12_ in the presence of pinacolborane.[55] Twenty examples of imines bearing various functional groups were investigated under this asymmetric catalytic system (2 mol % catalyst). The enantiomeric ratios are among the best reports in alkyl imine hydroborations with pinacolborane (the enantiomeric ratios were determined by HPLC analysis on a chiral stationary phase).[55]

Concurrently, Johnson and Speed reported 1,2,4,3-triazaphospholenes (TAPs) halide catalysts (**Figure 7e**) in imine hydroboration. A series of triazaphospholene halides and alkoxide were synthesized through the reaction between bulky amidrazones and phosphorus tribromide in the presence of triethylamine which cleanly provided triazaphospholene bromide. Triazaphospholene hydrides obtained subsequently under treatment with sodium benzyloxide in toluene.[56]

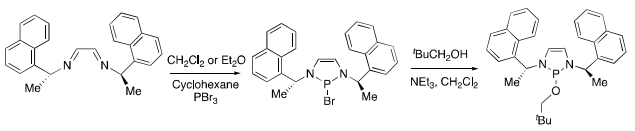
Triazaphospholenes are analogous to N-heterocyclic carbenes and yet there are few reports of them used in catalysis. Among the synthesized catalysts (**Figure 8**), pyrrolo triazaphospholene halides appeared to be the most effective due to the ease of isolation of the corresponding amidrazone in imine hydroboration.56 Nineteen imine substrates underwent hydroboration including those which contained cyclopropyl and alkyne groups. Heterocycles such as pyridine and furan were well tolerated under the reaction conditions.[56] Two pharmaceutical substrates (fendiline and rasagiline) were also demonstrated to undergo reduction using this protocol indicating its potential for applicability toward commercially important compounds.[56]

The mechanism of this reaction was probed through stoichiometric reactions and DFT calculations which indicated that phosphorus serves as a Lewis acid and there is a possible interaction between triazaphospholenes catalyst and imine (**Scheme 15**).[56] DFT calculations with the LC-ωPBE functional and the exchange-hole dipole moment (XDM) dispersion model indicated a possible interaction of HBpin with the nitrogen bearing a tert-butyl group. Subsequent hydride transfer through a six-membered transition state leading to complex **III** (**Scheme 15**) would be exothermic, with an activation barrier of 23.0 kcal/mol above complex **II**. Finally, the triazaphospholene cation is regenerated through B–N bond formation and dissociation of the borylated amine (modest barrier of 11.7 kcal/mol) (**Scheme 15**).[56]

Following the work of Johnson and Ferguson, the Melen group reported an example of a boron-based catalyst in imine reduction: tris(2,4,6-trifluorophenyl)-borane (2,4,6-BAr^F_9). This catalyst is capable of reducing aldimines via hydroboration.[57] A range of electron donating, withdrawing, electronically neutral, and aliphatic aldimines were reduced under low catalyst loading and mild reaction conditions. For example, N-benzylideneaniline gave great yield of 95% (by in situ ^{1}H NMR spectroscopy) to borylated amine at room



Scheme 13. The catalytic cycle and reaction mechanism of imine hydroboration by a silicon-amidinate catalyst, calculated at the PBE/TZVP level of theory with DFT. ΔG and ΔG# represent the Gibbs free energy of reaction and the Gibbs free energy of activation respectively. All values are in kcal/mol.[109]



Scheme 14. Synthesis of chiral diazaphospholene catalyst.[55]

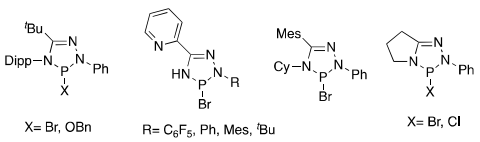
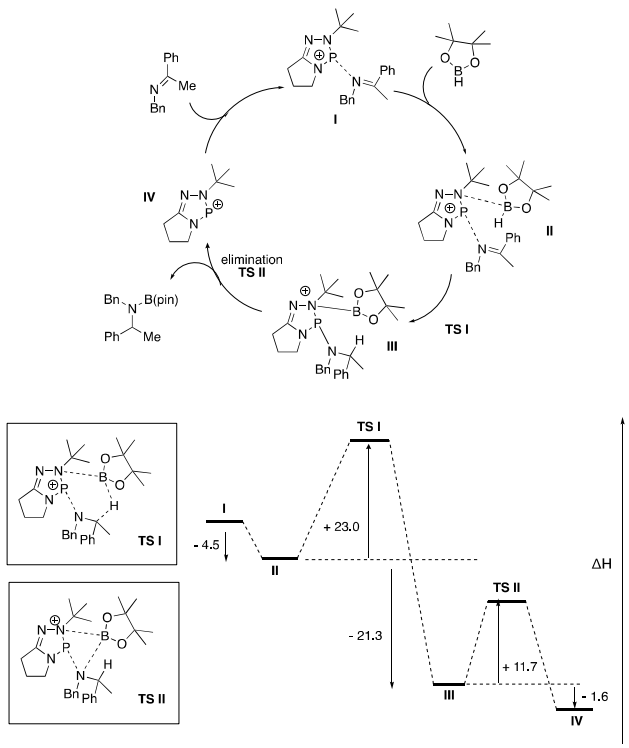


Figure 8. Synthesized triazaphospholene halides and alkoxide for imine hydroboration.[56]



Scheme 15. Proposed catalytic cycle and enthalpies calculated by DFT in triazaphospholenes catalyzed imine hydroboration. Energies given in kcal/mol relative to starting materials.[56]

temperature within 4 h. This Lewis acidic boron-based catalyst prevents any unwanted side-reactions with unsaturated frameworks in contrast to other Lewis acid boranes.[110]

Similarly, another boron Lewis acid, tris[3,5-bis-(trifluoromethyl)phenyl]borane (BAr^F_3), catalyzed imine hydroboration with pinacolborane (**Scheme 16**). The reaction enables effective hydroboration of both aldimines and ketimines within 18 h at room temperature This catalyst does not require an external Lewis base and gives moderate to excellent yield of 30-99%.[58] In comparison with other Lewis acidic boranes, BAr^F_3 was found to be much more reactive. The difference in catalytic activity can be attributed to decreased steric effects since both BAr^F_3 and $B(C_6F_5)_3$ have similar Lewis acidity (**Figure 9**).[111]

A broad scope of ketimine substrates with a range of substituents underwent efficient hydroboration to afford amine products after aqueous workup (77-99 % yield). Stoichiometric reactions between N,1-diphenylethan-1-imine and BAr^F_3 formed the expected Lewis pair $PhCCH_3$=NPh(BAr^F_3) in CD_2Cl_2 instantly. However, no reaction was observed between equimolar amounts of N,1-diphenylethan-1-imine and HBpin, as monitored by ^1H and ^{11}B NMR spectroscopy. Based on these findings and previous literature reports a proposed mechanism is presented in **Scheme 17**, which exclude the potential

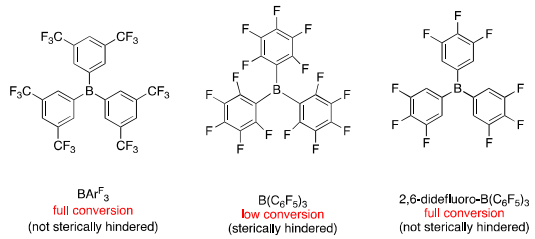
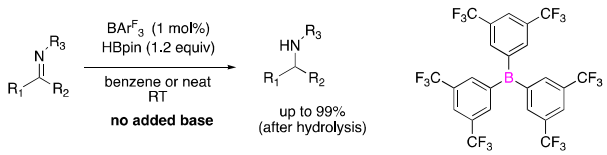
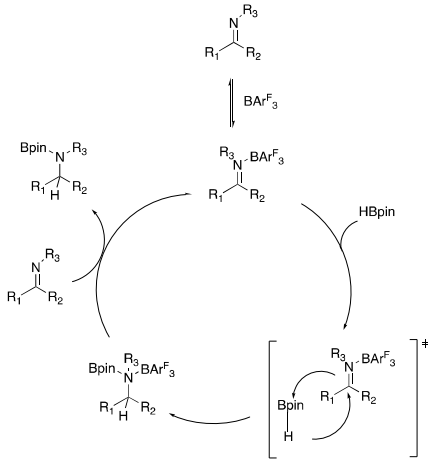


Figure 9. Boron Lewis acid catalysts.[111]



Scheme 16. Imine hydroboration catalyzed by Lewis acid tris[3,5-bis-(trifluoromethyl)phenyl]borane ($BArF_3$).[58]



Scheme 17. Postulated catalytic cycle for BAr^F_3 catalyzed imine hydroboration.[58]

formation of borenium ion as it was not observed in the NMR spectra.[58]

In 2018, the catalytic activity of aluminum complexes were studied in transformations such as C-C cross coupling,[112] catalytic hydroelementation such as alkyne and carbonyl hydroboration[113] etc. Following up on earlier reports, Mulvey and McLellan studied the catalytic activity of bimetallic lithium aluminates and neutral aluminum counterparts in hydroboration reactions. Hydroboration of N-benzylidenemethylamine under 10 mol % of Al complexes at room temperature revealed the bimetallic complexes to be more efficient than monometallic analogues. This was the first report of the use of Al complexes in catalytic imine hydroboration. In addition, benzophenone imine was reduced in higher yield (up to 80 %) in comparison to an aldimine substrate.[54] Stoichiometric experiments were carried out to gain insight into the reaction mechanism.

Results indicate that bimetallic lithium aluminate complexes h and i (**Figure 7)** proceeds through deprotonation. Proposed mechanism under catalyst i is depicted in **Scheme 18** which is started with deprotonation of benzophenone imine, followed by hydroboration and subsequently protonolysis to generate product and catalytically active species. The higher activity of bimetallic complexes is attributed to the key role of bimetallic (Li–Al) cooperativity in these complexes which increases the polarization of reaction intermediates. This study revealed the importance of anionic ate complexes among main group catalysts with higher conversion in shorter timescale.[54]

Later on in 2019, Xue group reported n-Butyllithium (n-BuLi) as catalyst in imines hydroboration. A wide scope of substrates (18 examples) studied under 6 mol % n-BuLi at room temperature within 1-24 h. Isolated yields of 76-91% obtained. However, most of the substrates were among aldimines. [114]

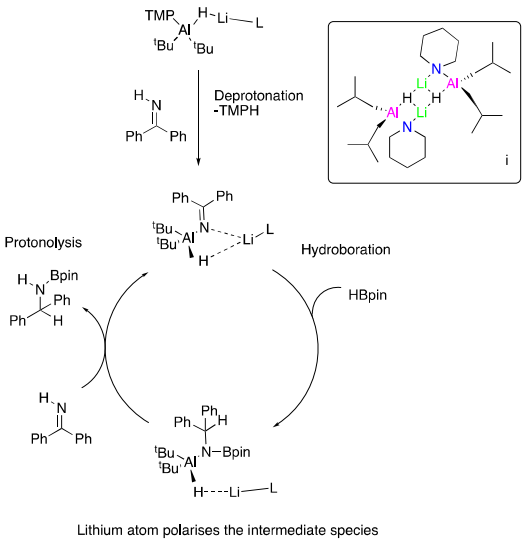
In the same year, Speed group reported diazaphosphenium triflate in asymmetric catalysis of cyclic imines via hydroboration. 0.2-1 mol % catalyst loading is used and enantiomeric ratios of up to 97:3 obtained to form aryl/heteroaryl pyrrolidines and piperidines (22 examples- at 35 °C). Enantiomeric ratios determined by HPLC on a chiral stationary phase with 71-94% isolated yields. This is the first example of an asymmetric reaction catalyzed by a phosphenium cation.[115]

In 2020, a mesoionic N-heterocyclic olefin (^{m}NHO) compound was developed and reported to be highly effective in imine hydroboration. Although, only two imine substrates were studied with this catalytic system.[116]

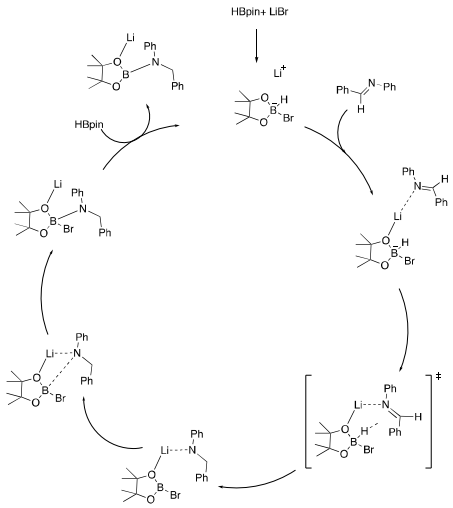
In the same year, the lithium bromide catalyzed imine hydroboration was also disclosed. N-benzylideneaniline was used as the model substrate with which to optimize the reaction conditions. This catalytic process was effective in a broad scope of substrate, both aldimines and ketimines bearing electron donating, withdrawing, electronically neutral substituents, and heteroatoms were reduced under mild low catalyst load (3 mol %) at room temperature. Chemoselective experiments with various functional groups (ester, amide, nitrile, alkene) revealed exclusive reduction of the imine moiety to form amine products. A plausible reaction mechanism was proposed using supporting DFT calculations (**Scheme 19**).[117]

In 2020, the same group reported a readily available NaH catalytic system for aldimine hydroboration. Only 3 mol % NaH was required for this transformation to form amine products under minimal solvent. The reaction is carried out in THF at 60 °C. This reaction time was considerably longer than the prior study. This protocol is chemoselective in the presence of other reducible groups, including esters, amides, nitriles, alkyl halides, and epoxide. The mechanism of the reaction also was elucidated by means of DFT calculations.[118]

A recent study described how protic additives (i.e., alcohols or water) can promote alkyl imine reduction with pinacolborane.[119] However, aniline derived imines were not found to be effectively reduced upon addition of a stoichiometric amount of alcohol or water. This can be attributed to the reduced basicity of the aniline derived imines. Furthermore, amine impurities can also promote imine reduction in some cases; a slow autocatalytic reaction.[119]



Scheme 18. Proposed mechanism for hydroboration of benzophenone imine catalyzed by i.[54]

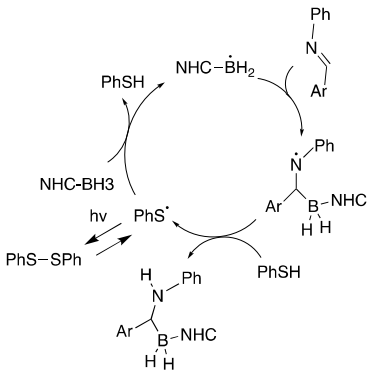


Scheme 19. Plausible mechanism of imine hydroboration using LiBr.[117]

In 2021, an inverse imine hydroboration was reported by Kawamoto group using NHC-boranes (1,3-dimethylimidazole borohydride). This hydroboration is free of photoredox catalyst and it is prompted by visible light irradiation of an acetonitrile solution of substrate in the presence of diphenyl disulfide (PhSSPh, 10 mol %). Relatively broad substrate scope (12 examples) were studies with high isolated yield of 69-95%. The mechanism is proposed through the radical chain reaction via a nucleophilic boryl radical (**Scheme 20**).[120]

In the same year, borane-dimethyl sulfide (Me_2S-BH_3) catalyzed hydroboration of imines was reported by Vidovi´c group. They proposed that Me_2S-BH_3 acts as a hydride donor in the reduction of various imines with good to moderate isolated yield of 44-88 % (14 examples).[121]

Noticeably, a catalyst free and solvent free imine hydroboration was report in 2019. This methodology is capable and compatible using 1.1-1.3 eq HBpin. Wide scope of aldimines ranging from electronically diverse and sterically hindered examples underwent reduction at ambient temperature. Although, the reaction time is longer as compared to catalyzed protocols (6-24h). Moreover, this catalytic system was unsuccessful in ketimine reduction under the same reaction condition (at room temperature). Ketimine hydroboration observed at higher temperature of 60 °C which was much less effective than previously reported catalyzed reactions. This protocol offers a chemoselective conversion of imine over alkene, alkyne, ketone, nitro, and nitrile.[66]



Scheme 20. Chain mechanism for the inverse hydroboration of imines.[120]

Table 5. Main group element catalyzed hydroboration of imines; Comparison of reaction conditions

Catalyst	Catalyst mol %	Solvent	Tem(°C)/ Time (h)	TON	TOF (h^{-1})	Ref
Borenium ion	5	$PhCF_3$	RT/45min-24h	19.2	19.2	105
Mg	5-10	C_6D_6	25-70/ 0.2-96	19.8	99	53
Si	1	CH_3CN	65/48-72	44	0.88	108
DAP (2017)	2	THF	25/16	47	3	55
TAP	0.1	THF	RT/16	937	58.5	56
2,4,6-$BArF_9$	2	CH_2Cl_2	RT-60/ 4-24	47.5	12	57
$BArF_3$	1	C_6D_6	RT/18	99	5.5	58
Al-Li	5	C_6D_6	RT/0.5-2	14	29	54
^{m}NHOs	2	THF	70/12	48.5	4	116
LiBr	3	THF	RT/1	32	32	117
NaH	3	THF	60/24	33	1.37	118
PhSSPh	10	CH_3CN	CFL(12W)/14h	9.9	0.71	120
n-BuLi	6	THF	RT/1h	16.5	16.5	114

3. Hydroboration of nitriles

3.1. Transition metal catalyzed hydroboration of nitriles

The reduction of nitriles to primary amines has been carried out through hydroelementation reactions such as hydroboration and hydrosilylation. Like imines, this method resolves the problems associated with high-pressure setups, eliminates the generation of inorganic wastes, and possesses improved selectivity. Nitrile hydrosilylation forms both the monosilylated imine and disilylamine products; however, hydroboration produces the diboronate amine selectively.[47] Nitriles have a strong C=N bond dissociation energy (750.0 kJ/mol) which make them hard to reduce under the typical reaction conditions.[82] However the presence of a catalyst facilitates the process.

The first catalytic nitrile hydroboration was reported by the Nikonov group in 2012. An imido-hydrido complex of Mo (IV) was developed and deployed in the hydroboration of acetonitrile and benzonitrile using catecholborane. Reaction progress was monitored employing ^{1}H NMR which indicated complete conversion was achieved in the presence of 5 mol % catalyst within 12 h at 22 °C.[67]

To date, more than a dozen transition metal catalysts have been reported to be effective in nitrile hydroboration. In 2015, a series of proton-switchable bifunctional ruthenium complexes was introduced by Szymczak group.[75] These metal complexes contain pincer ligands. At 5 mol % loading the Ru complex (example Figure 10 b) could convert nitrile substrates to borylated amines in the presence of 2 eq

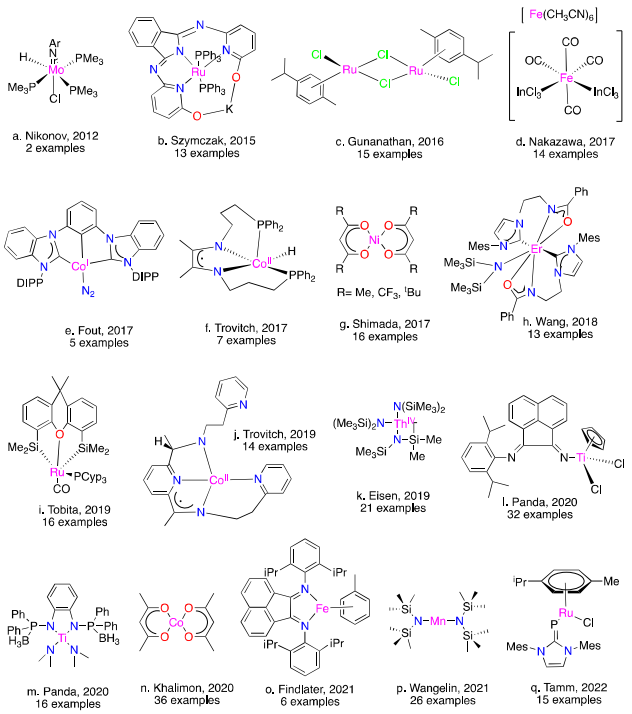
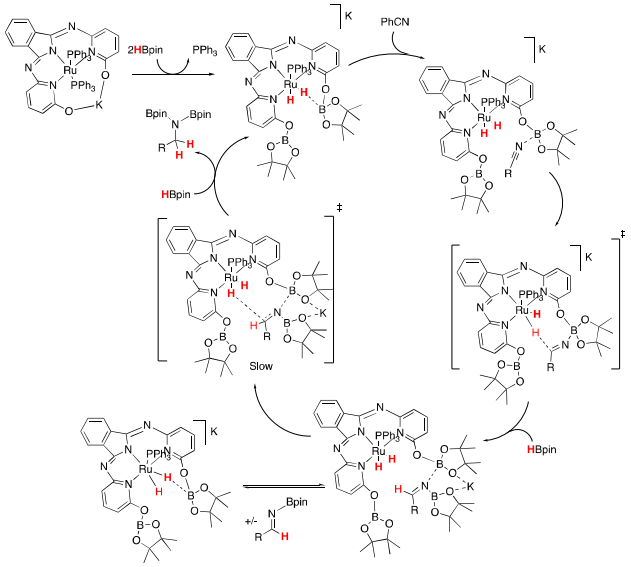


Figure 10. Transition metal catalysis in nitrile hydroboration.

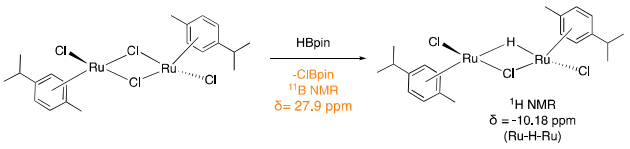
HBpin and C_6D_6 as solvent. A wide range of *p*-substituted aryl nitriles can thus be hydroborated in moderate to excellent yields. Functional groups such as methyl esters, trifluoromethyl, 2-pyridyl, benzyl ethers and 2-furyl were all well tolerated. In addition, stoichiometric reactions with H_2 and HBpin revealed B-H bond activation and is facilitated through Ru^{II}-O bond.[75] This provides Ru−H species available for reaction with the neighboring atoms. The reaction is also revealed to be first order with respect to catalyst and zero order in both HBpin and benzonitrile. This proposed reaction mechanism is presented in **Scheme 21** depicting the critical role of the bifunctional ligand in the reaction: (1) B-H bond heterolysis, (2) Bpin binding to oxygens of the ligand and cooperative interaction with substrate, and (3) a proton-switchable assist at the metal center.[75]

Another example of Ru catalyzed nitrile hydroboration was reported by the Gunanathan group in 2016 (**Figure 10c**). Using 1 mol % of a commercially available $[RuCl_2[p\text{-cymene})]_2$ catalyst, diboryl amines could be prepared under solvent-free conditions at 60 °C. The reaction proceeds via the in situ formation of imines.[47] Interestingly, this catalyst is capable of the chemoselective hydroboration of nitriles over esters. Moreover, stoichiometric reaction between the Ru complex and HBpin produces a singlet resonance in the metal-hydride region (δ_{Ru-H} = −10.18 ppm) which confirms the immediate formation of a mono hydrido-bridged dinuclear complex of form: [{(η^6-p-cymene)- RuCl} (μ-H-μ-Cl)] in the reaction mixture (**Scheme 22**).[47]

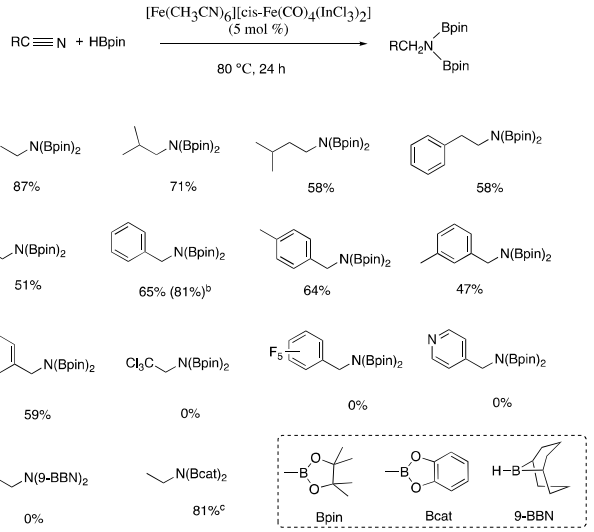
An iron−indium cooperative catalyst was introduced by Nakazawa: $[Fe(CH_3CN)_6][cis\text{-}Fe(CO)_4(InCl_3)_2]$. The double hydroboration of organonitriles could be accomplished with 5-10 mol % of this iron-indium catalyst using several different reducing agents HBpin, HBcat and 9-BBN at 80 °C within 24h. Both aliphatic and aromatic substrates underwent hydroboration with good to moderate isolated yields of 47-87% (**Scheme 23**). A plausible reaction mechanism is presented in **Scheme 24** and involves the dissociation of one $InCl_3$ of the catalyst to afford a monoindium iron complex. Subsequent ligand exchange occurs between CO and the organonitrile substrate.[122]



Scheme 21. Proposed mechanism in Ru catalyzed nitrile hydroboration.[75]



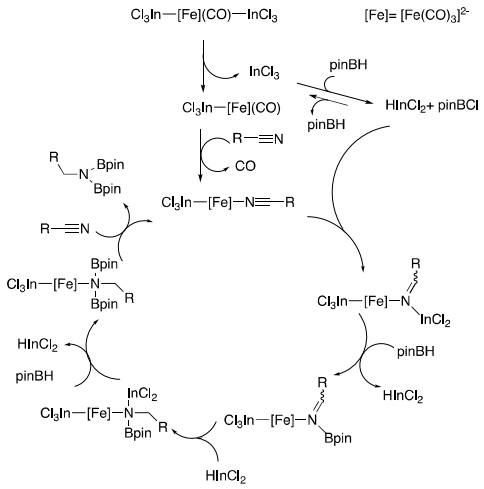
Scheme 22. Mono hydrido-bridged dinuclear complex of [{(η^6-p-cymene)-RuCl}(μ-H-μ-Cl)] in nitrile hydroboration.[47]



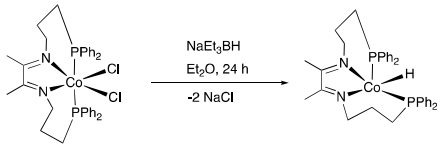
Scheme 23. Double hydroboration of organonitriles in the presence of $[Fe(CH_3CN)_6][cis\text{-}Fe(CO)_4(InCl_3)_2]$.[122]

Several base metal catalysts were reported in 2017, among them examples of Co[123] and Ni[124] complexes. The Fout group reported a Co^I system which was effective in catalytic nitrile double hydroboration (**Figure 10e**).[123] The scope of substrate explored in this report was limited (5 examples). The highest yield reported was 85% in the hydroboration of 3,5-difluorobenzonitrile where the product was isolated as the corresponding ammonium salt.[123]

Later in the same year, an interesting tetradentate α-diimine cobalt hydride catalyst was reported by the Trovitch group.[73] This catalyst was prepared from the addition of $NaEt_3BH$ to the precursor dihalide complex, (^{Ph2PPr}DI)$CoCl_2$ (**Scheme 25**). X-ray diffraction experiments and DFT calculations revealed that the monohydride, (^{Ph2PPr}DI)CoH complex (**Scheme 25)** contains a radical monoanion α-diimine ligand and a Co(II) center with a distorted square pyramidal geometry.[73]



Scheme 24. Proposed catalytic cycle for double hydroboration of organonitriles in the presence of $[Fe(CH_3CN)_6][cis\text{-}Fe(CO)_4(InCl_3)_2]$ catalyst.[122]



Scheme 25. Monohydride cobalt catalyst in nitrile hydroboration.[73]

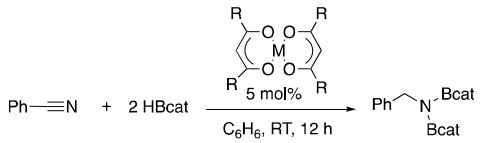
Addition of 1 mol % of the Co hydride catalyst to nitrile substrates in the presence of HBpin afforded the corresponding diboryl amines in good to moderate isolated yields of 30-88% within 24 h.[73]

The Shimada group employed commercially available nickel salts of bis(acetylacetonato)nickel(II) and found them to be highly effective in nitrile hydroboration.[124] Initially, the catalytic activity of different metal salts in hydroboration of benzonitrile with HBcat at room temperature was explored (**Table 6**).[124] Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II)) (**Table 6**-entry 3) was revealed to be the most effective catalyst amongst other metal salts. Nitriles with various functional groups underwent reduction with excellent yield up to 95 % isolated yield under 0.5-5 mol % catalyst loading with HBcat (benzene as solvent/ at room temperature). The proposed reaction mechanism is presented in **Scheme 26** which is through oxidative addition of Ni(0) species to HBcat, leading to the formation of boryl hydride intermediate.[124]

In 2018, an N-heterocyclic carbene-supported complex of Er was disclosed by the Wang group. This rare-earth metal catalyst (2 mol %) was found to exhibit excellent catalytic activity (89-99% isolated yield) in nitrile hydroboration in toluene.[50]

The Tobita group reported a Ru complex to be an effective catalyst in nitrile hydroboration. This 16-electron ruthenium complex bears a bis(silyl)xanthene chelate ligand xantsil; Ru[k_3(Si,O,Si)-xantsil](CO)($PCyp_3$) (Cyp = cyclopentyl).[74] Interestingly, this complex functions as a catalyst in both double and single hydroboration of nitriles. HBpin and 9-BBN (9-borabicyclo[3.3.1]nonane) were

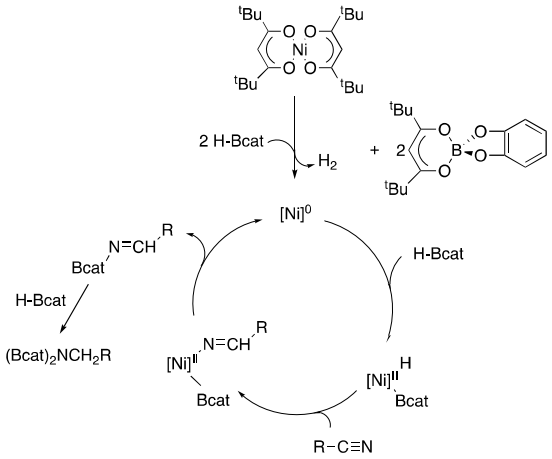
Table 6. Hydroboration of PhCN with HBcat catalysed by different metal salts.[124]



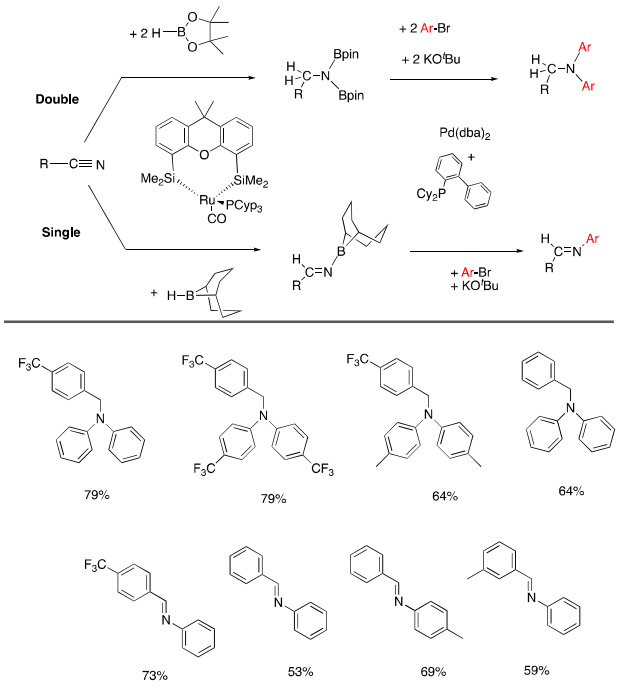
Entry	Catalyst	Yield[b]
1	$Ni(acac)_2$	>99(49)[c]
2	M= Ni, R=CF_3	>99(19)[c]
3	M= Ni, R=^{t}Bu	>99(78)[c]
4	$NiCl_2$	ND
5	$Ni(cod)_2$	87
6	$Co(acac)_2$	37
7	$Cu(acac)_2$	ND
8	$Mn(acac)_2$	ND
9	$Pd(acac)_2$	ND

[a]Catalyst (0.01 mmol), PhCN (0.20 mmol), and HBcat (0.44 mmol) in 5 mL C_6H_6 at room temperature for 12 h. [b] NMR yield based on an internal standard ($PhSiMe_3$). [c]The values in parenthesis represent the yields at a 1 mol % catalyst loading.

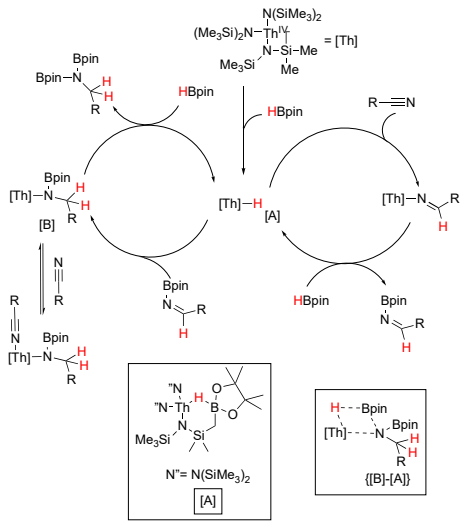
employed to form bis(boryl)amines and N-borylimines, respectively in mostly excellent yield up to 99 %. Beyond the hydroboration pathway, this study also describes deborylative C–N coupling reactions of borylated amines utilizing $Pd(dba)_2$ (dba=dibenzylideneacetone) as catalyst (**Scheme 27**).[74, 125]



Scheme 26. Possible mechanism of hydroboration of nitrile catalyzed by bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II).[124]



Scheme 27. One-pot synthesis of N,N-diarylamines or N-arylimines from nitriles by double or single hydroboration and C-N coupling.[74] Conditions for synthesis of bis(boryl)amines: nitrile (0.29 mmol), HBpin (0.63 mmol), Ru catalyst (7 µmol, 2 mol %), 40–60 °C, THF; bromoarenes (0.61 mmol), KO^{t}Bu (0.61 mmol), Pd(dba)$_2$ (6.1 µmol, 2 mol %), CyJohnPhos (14 µmol, 5 mol %), 60 °C, 12 h, THF. Conditions for synthesis of N-borylimines: nitrile (0.099–0.29 mmol), 9-BBN (0.12–0.32 mmol for the monomer), Cat. (0.7–1.4 µmol, 0.5–0.7 mol %), 1 h, rt, THF; bromoarenes (0.11–0.32 mmol), KO^{t}Bu (0.12–0.32 mmol), Pd(dba)$_2$ (2.1–6 µmol, 2 mol %), CyJohnPhos (4–14 µmol, 4–8 mol %), 60 °C, 12 h, THF. Isolated yields based on nitriles.



Scheme 28. Proposed mechanism for Th catalysed hydroboration of nitriles.[49]

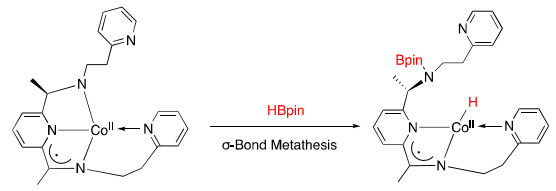
A complex of the actinide thorium was recently introduced by Eisen and coworkers as a nitrile hydroboration catalyst (**Figure 10k**).[49] This metallacyclic thorium amide complex, [(Me$_3$Si)$_2$N]$_2$Th[κ$_2$–(N,C)–CH$_2$Si(CH$_3$)$_2$N(SiMe$_3$)], is highly effective in nitrile hydroboration with very good TOF of up to 500 h^{-1}. A wide scope of substrates bearing different functional groups were studied under low catalyst loading (0.1 mol %) with excellent yields (75-100%).[49]

The mechanism of this reaction was studied using kinetic, stoichiometric, and temperature dependence experiments. Taken together, these results were interpreted to generate a proposed mechanism in which a facile activation of the precatalyst occurs via insertion of the HBpin into the thorium metallacycle to afford the active thorium hydride complex as depicted in **Scheme 28**. The activation parameters for the hydroboration of PhCH$_2$CN were determined from Eyring and Arrhenius plots. ($\Delta H^{\ddagger}$= 6.99 (0.44) kcal/mol $\Delta S^{\ddagger}$=47.25(1.23) e.u., E_a= 7.66(0.44) kcal/mol).[49]

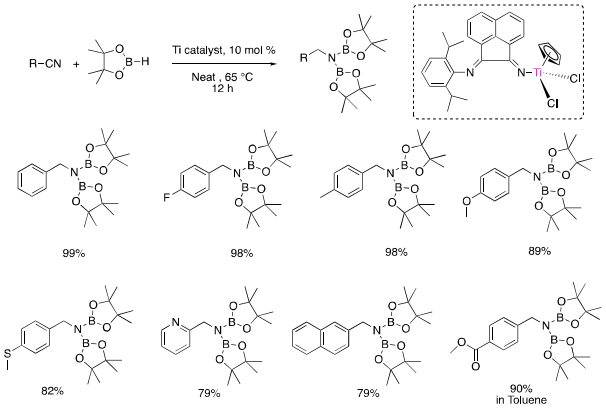
In the same year, another report of cobalt catalyzed nitrile hydroboration was disclosed by the Trovitch group.[126] This low-spin Co(II) catalyst (1 mol %) is capable of the hydroboration of nitrile substrates efficiently with TOF of up to 380 h^{-1}. 14 nitrile examples were reduced under this method with mostly excellent yields obtained at ambient temperate within 2 h. DFT calculations reveals catalyst activation to occur through a Co–N bond hydroboration, implying that through the course of the catalytic cycle all steps involve high-spin Co(II)-species (**Scheme 29**).[126]

Recently, the Panda group reported examples of Ti catalysts in nitrile hydroboration. These were the first reports of titanium acting as catalyst in the synthesis of organo-boron compounds (**Scheme 30-32**).[77, 127] The titanium amido bond in these catalysts are labile allowing the facile formation of a metal hydride (**Scheme 30 & 31**).[127] The metal hydride species can effectively catalyze the hydroboration of unsaturated C-X bonds. Hydroboration of nitriles proceeds in excellent yield in neat conditions under 10 mol % catalyst loading at 65 °C. A wide scope of substrates bearing electron donating, electron withdrawing, neutral, and heteroatoms are reduced in 80-99% yield within 2-10 h using both HBpin and HBcat Hydrolysis of diboryl amine products was performed under treatment with 0.05 M aqueous HCl for 4 h at room temperature to afford the corresponding amines.[127]

A cobalt catalyzed nitrile hydroboration reaction was reported by the Khalimon group in 2020. This group utilized the commercially available Co(acac)$_2$ (acac= acetylacetonate) in conjunction with dpephos (Bis[(2-diphenylphosphino)phenyl] ether) ligand in nitrile hydroboration at ambient temperature. N,N-diborylamines contain labile B-N bonds and can be utilized in the synthesis of a variety of N-containing organic molecules[128]. To this end, a one-pot transformation of nitriles to aldimine was achieved via hydroboration and subsequent in situ reaction of diborylamine with aldehydes to give aldimines. The aldimine products were purified by flash column chromatography using silica gel neutralized with NEt$_3$.[128]



Scheme 29. Co(II) hydride species in nitrile hydroboration.[126]



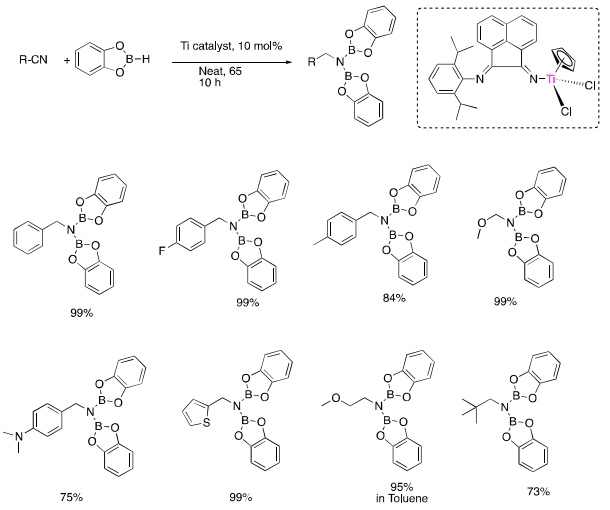
Scheme 30. Selected examples of Ti catalyzed double hydroboration of nitriles in the presence of HBpin.[127] Reaction conditions: catalyst (10 mol %), nitrile substrates (1 eq.), HBpin (2.2 eq.). The reaction mixture was heated to 65 °C. Isolated yields

Khalimon and co-workers proposed that the reaction mechanism proceeds through the formation of a (dpephos)Co^{I}-H species.[128] This would involve the migratory insertion of a bound nitrile into the Co-H bond and the subsequent reaction with HBpin to generate the N-borylimine RCH=N(Bpin). This species subsequently undergoes insertion into the Co-H bond to yield N-borylamide and finally the N,N-diborylamine (**Scheme 33**).[128]

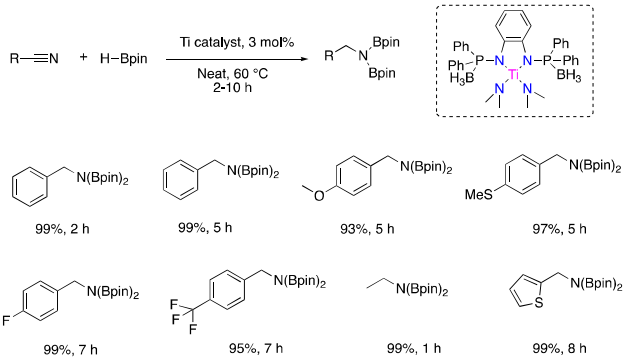
Very recently in 2021, Wang and Guo reported a mixture of cobalt (II) iodide and potassium tert-butoxide to be effective in double hydroboration of nitriles.[129] The alkoxide-pinacolborane combination activates cobalt(II) iodide to generate a metastable heterotopic cobalt catalyst *in situ* employing 0.5-2 mol % CoI_2 and 10 mol % KO^{t}Bu.

A wide range of aliphatic and aromatic nitriles were studied and isolated yields (as ammonium salts) as high as 99% could be achieved; catalytic reaction mixtures were stirred under N_2 at 30 °C for 4-24 h. Substrates with reductive groups of formyl and acetyl was further investigated. Both the cyano and carbonyl groups were reduced under standard conditions with a moderate yield of 74% and 64% of the doubly reduced product, respectively.[129]

Another base metal catalyst deployed in nitrile diborylation was reported by Findlater group using ^{dpp}BIANFe(Tol) precatalyst (1 mol %) under solvent-free and additive-free conditions (70 °C or RT).



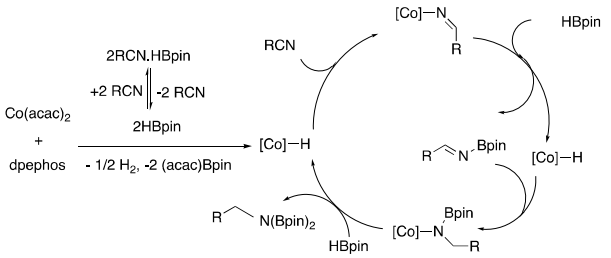
Scheme 31. Selected examples of Ti catalyzed double hydroboration of nitriles in the presence of HBcat.[127] Reaction conditions: catalyst (10 mol %), nitrile substrates (1 eq.), HBcat (2.2 eq.). The reaction mixture was heated at 65 °C. Yields were calculated based on ^{1}H NMR (400 MHz) integration of characteristic product peak using 50 mol % of 1,3,5-trimethoxybenzene as an internal standard.



Scheme 32. Selected examples of Ti catalyzed double hydroboration of nitriles in the presence of HBpin.[127] Reaction conditions: catalyst (3 mol %), nitriles (1 eq.), HBpin (2.2 eq.), neat condition at 60 °C; yield was calculated by 1H NMR (400 MHz) with respect to HMB (15 mol %) as the internal standard.

A small substrate scope was studied. The reaction was found to tolerate bromo- and chloro-substituents and aliphatic (cyclic) substrates. All substrates studied afforded diborylated amines in good to excellent yields of 84-99%. Products can be conveniently isolated as ammonium salts.[102]

Subsequently, manganese catalyzed hydroboration of nitriles introduced in 2021.[130, 131] Wangelin group reported manganese bis(hexamethyldisilazide) as precatalyst in nitrile dihydroboration under mild reaction condition (5 mol % $Mn(hmds)_2$, 20 °C within 20 h). Broad scope of aromatic and aliphatic nitrile substrates studied to form primary amines under this protocol with high yields (26 examples, 36-99%). Study of the reaction mechanism revealed the efficient catalytic activity resides in the ability of the metal center to



Scheme 33. Proposed mechanism for $Co(acac)_2$ catalyzed hydroboration of nitriles.[128]

act as Lewis acid. This is corroborated by isolation of an adduct upon the reaction between $Mn(hmds)_2$ and PhCN in hexanes.[131]

In 2022, Tamm group reported N-heterocyclic carbene-phosphinidene complex of Ru ([(η^6-*p-cymene*){(IMes)P}RuCl) in nitrile hydroboration. 2.1 eq. HBpin is used under 3 mol % catalyst loading and neat condition at 60 °C for 11 h. Isolated yield of borylated amines are reported (82-99%_15 examples). Preliminary mechanistic, kinetic studies and stoichiometric reactions revealed the initial formation of monohydride complex of [(η^6-p-cymene){(IMes)P}RuH] as the catalytically active species.[132]

3.2. Main group element catalyzed hydroboration of nitriles

The first example of a main group catalyst in nitrile hydroboration was introduced by Hill and co-workers in 2016 with the report of a single β-diketiminato n-butylmagnesium precatalyst. In this work, 15 nitrile examples underwent hydroboration using 10 mol % catalyst at 60 °C, over 0.5-30 h with good to excellent isolated yields (43-96%). Dihydroboration reaction was facile for 1-cyanoethyl substrate with isolated yield of 70% within 0.5 h. A sluggish reaction was observed in the case of diphenylacetonitrile substrate (43% after 30h) which was attributed to steric encumbrance at the substrate.[71]

The Panda group reported an aluminum alkyl complex precatalyst in 2018 capable of nitrile hydroboration to afford diborylamines under solvent-free conditions and mild temperatures (60 °C).[133] This aluminum complex was prepared by the treatment of [2-F-$C_6H_4NHP(Se)Ph_2$] and $AlMe_3$ in toluene (**Scheme 34**).[133]

In this work, an extensive range of substrates (up to 30 examples) were studied under this protocol using both HBpin and HBcat as the borylating agent (**Scheme 35 & 36**).[133] The end products were isolated using aqueous HCl (0.05 M) at room temperature for two hours, which gave a fine white powder of substituted benzyl ammonium chloride (**Scheme 37**). Moreover, the reaction mechanism is proposed through the formation of an aluminum hydride as the active species.[133]

In the same year, an unsymmetrical magnesium(I) β-diketiminate complex was synthesized by the Ma group. This alkaline earth-based catalyst was found to be effective with various nitrile substrates for hydroboration with a range of functional groups. Surprisingly, this complex has good solubility even in hexanes which makes it a highly efficient catalyst in almost all organic solvents.[134]

A year later, in 2019, closely related Al catalysts were independently reported by Ma and Yang [31] and Roesky[82] almost simultaneously. These groups employed (^{Dipp}NacNac)Al(Bu)$_2$ and (EtPhNacNac)AlH_2 as efficient catalysts in nitrile hydroboration under solvent free conditions.[31, 82] These reactions can be used to convert both aliphatic and aromatic nitriles to the corresponding N,N-diborylamines with 2 eq. HBpin and 3–5 mol % catalyst loading with good to excellent yields. (^{Dipp}NacNac)Al(Bu)$_2$ is comparatively more effective as the yields are typically greater than 90% for all substrates studied. The reaction was equally effective for both aliphatic and aromatic substrates. (^{Dipp}NacNac)Al(Bu)$_2$ catalyzed hydroboration was shown to be less sensitive to the electronic and steric properties of nitrile substrates which afforded higher yields and milder reaction conditions (60 °C, 0.25–4 h as compared with 80 °C, 6–24h). Both methods are believed to proceed through a key nitrile insertion step into the Al-H bond of the catalytically active species.[31, 82]

A well-defined aluminum dihydride complex bearing conjugated bis-guanidinate ligand was reported as catalytically relevant in nitrile dihydroboration by the Nembenna group in 2020. This conjugated bis-guanidine (CBG) supported aluminum dihydride complex was synthesized via treatment of CBG free ligand, LH, with 1 eq of Alane, $H_3Al{\cdot}NMe_2Et$ in toluene at 80°C (**Scheme 38**).[135]

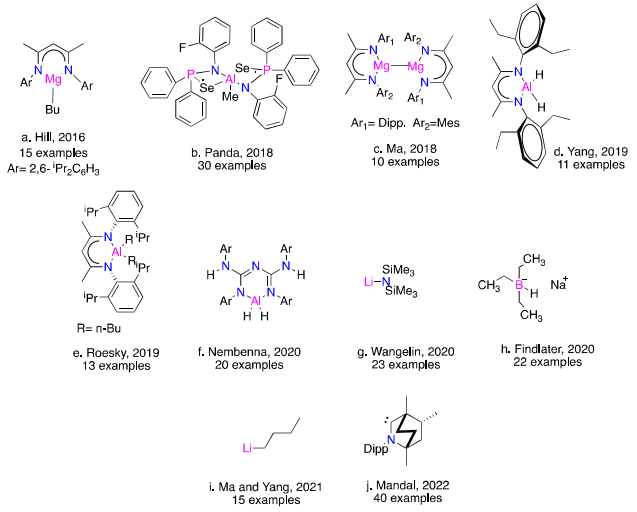
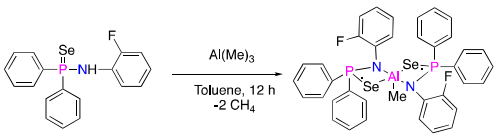
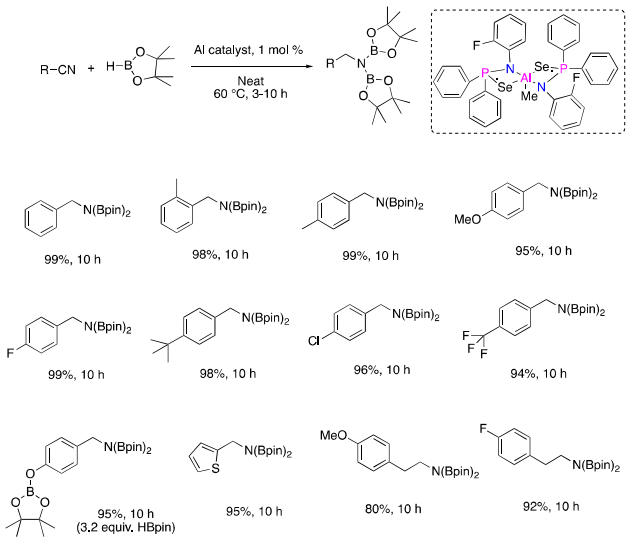


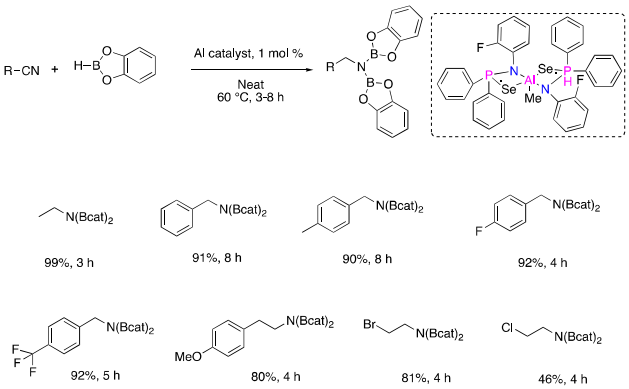
Figure 11. Reported main group element catalysts in nitrile hydroboration.



Scheme 34. Synthesis of aluminum (III) complex.[133]



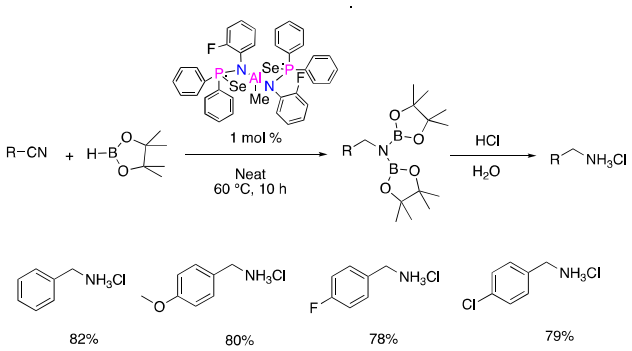
Scheme 35. Selected examples of Aluminum-catalyzed hydroboration of nitriles with HBpin.[133] Reaction conditions: Al catalyst (1 mol %), nitrile (1 eq.), HBpin (2.2 eq.), yield was calculated via ^{1}H NMR (400 MHz) integration of characteristic product signal present in the reaction.



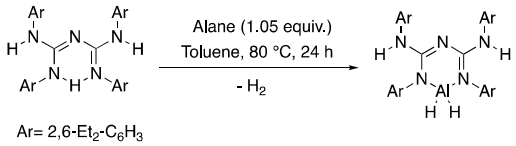
Scheme 36. Selected examples of Aluminum-catalyzed hydroboration of nitriles with HBcat.[133] Reaction conditions: Al catalyst (1 mol %), nitriles (1 eq.), HBcat (2.2 eq.), Yield was calculated based on ^{1}H NMR

In this case, catalytic studies were initiated with the model substrate benzonitrile which was used to optimize reaction conditions. For the model system, a 97% yield was obtained under 3 mol % catalyst loading, 2 eq HBpin at 60 °C with neat conditions.

A wide range of organic nitriles were investigated using this catalytic approach, a number of diverse substituents such as OMe, Cl, and F are all well tolerated.[135] Substrates bearing the reducible carbonyl functional group were incompatible with this system. These reactions resulted in 83% and 52% diborylated products using



Scheme 37. Hydrolysis of diborylamines to primary amines.[133]



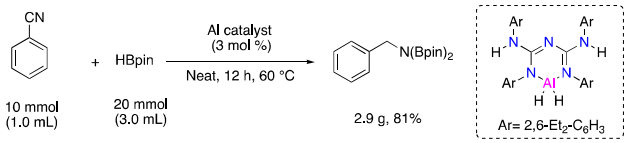
Scheme 38. Synthesis of conjugated bis-guanidinate supported aluminum dihydride complex.[135]

4-formylbenzonitrile and 4-acetylbenzonitrile as substrates respectively. Moreover, gram-scale hydroboration of benzonitrile (1 g) was also successful (**Scheme 39**). The mechanism of this reaction is proposed to proceed through the formation of an intermediate imine complex followed by association of HBpin to the Al center and addition of H-B across the Al-N bond via a four-membered transition state (**Scheme 40**). In addition, the stoichiometric reaction between the catalyst and trimethylacetonitrile in $CDCl_3$ at 70 °C provided supporting evidence for the postulated aluminum imine intermediate.[135]

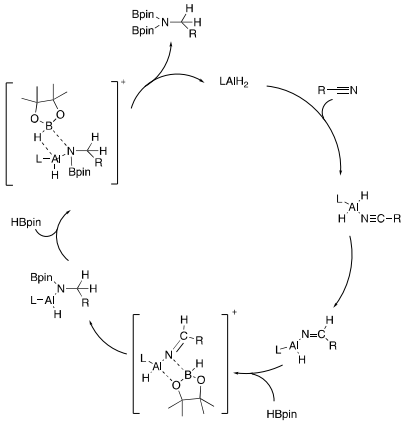
Subsequently, the von Wangelin group reported lithium hexamethyldisilazide ($LiN(SiMe_3)_2$ or Li(hmds) as a catalyst in nitrilehydroboration. Here, the optimized reaction conditions were found to be 10 mol % catalyst loading at 20-70°C to obtain yields range of 64-99% for both aromatic and aliphatic substrates within 20 h.[136] This readily available compound is suitably Lewis acidic to activate the nitrile substrates while also Lewis basic enough to convert the borane to an-ate complex.[136] Various alkali metal alkoxides and amide bases with bulky groups were studied in benzonitrile hydroboration, and ($LiN(SiMe_3)_2$ gave excellent yields of 70-96 % of the desired benzylamine products at room temperature.[136] Further optimization of the reaction using various borylating reagents such as $NH_3{\cdot}BH_3$, $NMe_3{\cdot}BH_3$, HBpin and HBcat identified HBpin to be the most suitable. A broad substrate scope was investigated and the conditions were found to tolerate iodo-, bromo-, and thiomethyl-substituents even in the presence of heteroarenes such as thiophene, furan, and pyridine.[136] However, higher temperatures were required to facilitate reactions of the electron-rich 4-N,N-dimethylaminobenzonitrile and the bulky ortho-tolunitrile. Additionally, the reaction is highly chemoselective for nitriles over styrenic substrates. Kinetic studies revealed a first order rate with respect to both lithium catalyst and nitrile. The proposed mechanism is based upon stoichiometric and kinetic analysis and

invokes the formation of Lewis acid-base adduct, the amidinate [RC(NSiMe$_3$)$_2$Li•NCR] (**Scheme 41**).[136]

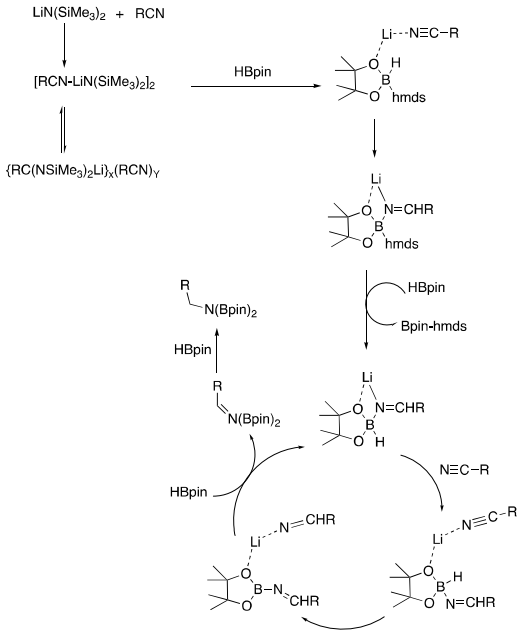
A highly efficient solvent-free double hydroboration of nitriles was reported by the Findlater group in 2020. Commercially available sodium triethylborohydride was employed as the catalyst and diboryl amine products were easily obtained in up to 99% yield using 5 mol % catalyst. An array of substrates (22 examples) was reported to undergo facile hydroboration. Substrates with aliphatic and aromatic groups, and heteroatoms underwent hydroboration with excellent isolated yields of 74-99%. High TOF of 2400 h^{-1} is obtained in hydroboration of 4-(Trifluoromethyl)benzonitrile. However, there is no reaction for substrates with nitro and pyridine groups which could be the result of inductive effects from nitrogen atoms in the backbone of the substrate which disfavor the formation of B-N bond. The mechanism of the reaction was probed through the independent preparation of the proposed boryl-imine intermediate, and the subsequent addition of a second equivalent of HBPin.[69]



Scheme 39. Large-scale hydroboration of benzonitrile with HBpin.[135]



Scheme 40. Proposed mechanism for hydroboration of nitrile using Al catalyst.[135]



Scheme 41. Proposed reaction mechanism of Li catalyzed hydroboration of nitriles in the presence of HBpin.[136]

In 2021, Ma and Yang reported n-BuLi (5 mol %) as an efficient catalyst in nitrile dihydroboration with HBpin under solvent-free condition. Broad substrate scope (15 examples) with good functional group compatibility were studied with NMR yield of 78-99% at 60 °C within 3-12h. Large scale synthesis went successful with 89% yield of benzonitrile. In addition, high chemoselectivity of imine over nitrile reduction was observed under this procedure.[137]

Very recently in 2022, Mandal group reported a Bicyclic (alkyl)(amino)carbene (BICAAC) catalyst in metal free and solvent free hydroboration of nitriles. A wide scope of substrates including aromatic, heteroaromatic, and aliphatic nitriles (40 examples) were studied using 5 mol % catalyst with 30-92% isolated yield as ammonium salt. Gram-scale synthesis of benzonitrile was also successful with 70% isolated yield. Mechanism of the reaction studied using both experiments and DFT calculations which suggest the B-H addition to the carbene center, as hydride source.[138]

4. Main group and transition metal catalyzed hydroboration of carbodiimides

The first example of carbodiimide hydroboration was reported in 2011 by the Xia group. In this work, 1-H-boratabenzene rare-earth metal complexes of Yttrium (Y) or Lutetium (Lu) efficiently catalyzed hydroboration of carbodiimide substrates. The presence of a B-H bond makes this complex special as the B-H bond is much more reactive than the analogous C-H bond. Hydroboration of N,N'-diisopropylcarbodiimide with the Yttrium complex of [C$_5$H$_5$BH]$_2$YCl yields boratabenzene yttrium chloride [C$_5$H$_5$BN-

(^{i}Pr)CHN(^{i}Pr)][C_5H_5BH]YCl in 90% at room temperature (**Scheme 42**). Another 1-H-boratabenzene complex was synthesized using lutetium, $[C_5H_5BH]_2LuCl$. Catalytic hydroboration of N,N′-diisopropyl-carbodiimide was also performed successfully in 87% yield at room temperature. However this report was limited to a single substrate.[104]

In 2016, more extensive research on carbodiimide hydroboration was reported by the Hill group. Alkyl- and aryl-substituted carbodiimides were studied using a *β*-diketiminato magnesium alkyl complex, [CH{C(Me)NDipp}$_2$}Mg^{n}Bu]. Substrates with reduced steric hindrance provided more efficient conversion to the desired products.

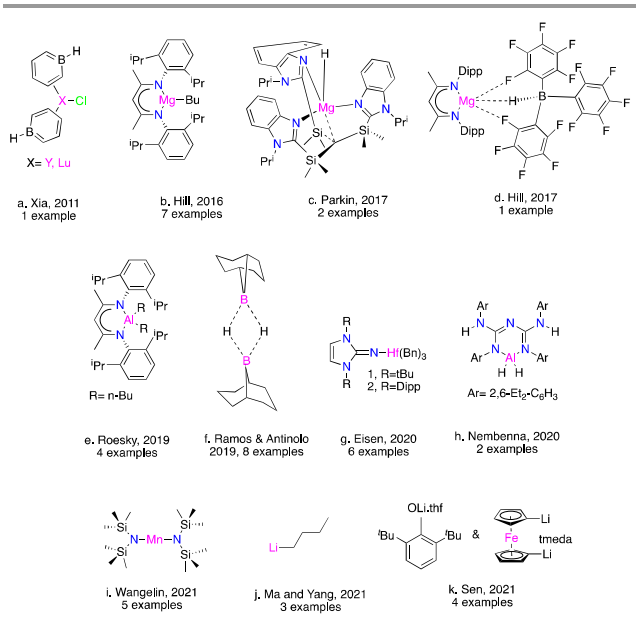
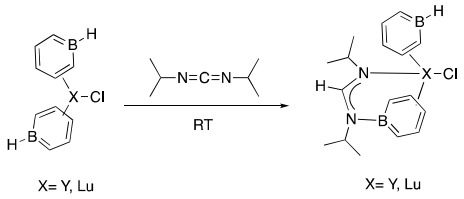
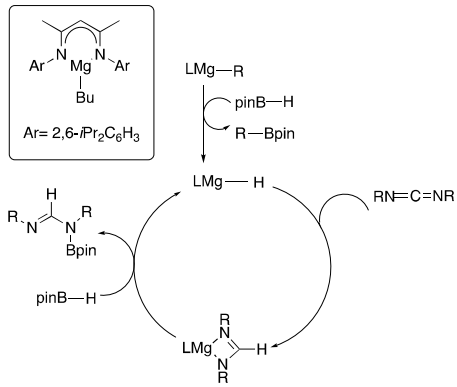


Figure 12. Highlighted reported catalysts in carbodiimide hydroboration.



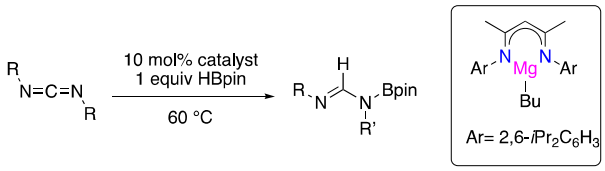
Scheme 42. Hydroboration of N,N′-diisopropylcarbodiimide with 1-H-boratabenzene rare-earth metal complexes.[104]

Prolonged reaction times and elevated temperatures were required when using substrates with bulky groups (**Table 7**). The reaction is proposed to proceed through B-H/Mg-C metathesis to initiate the catalytic reaction. This is then followed by the formation of hydridomagnesium species (**Scheme 43**).[139]



Scheme 43. Proposed mechanism in Mg catalyzed carbodiimide hydroboration.[139]

Table 7. Magnesium-catalyzed hydroboration of commercially available carbodiimide.[139]



Entry	R, R'	t (h)	T (°C)	Conv. (%)[a]	Yield (%)[b]
1	^{i}Pr	15	60	90	89
2	Cy	15.5	60	90	69
3	^{t}Bu	60	80	88	87
4	2,6-i$Pr_2C_6H_3$	24	80	80	77
5	*p*-$CH_3C_6H_4$	15	80	81	63
6	^{t}Bu, Et	20	60	75	87
7	$(CH_2)_3NMe_2$, Et	5.5	60	90	87

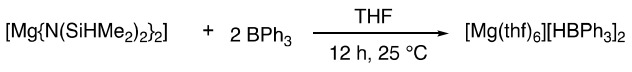
[a]Determined by ^{1}H NMR spectroscopy in C_6D_6. [b]Preparative-scale experiments performed in toluene.

In 2017, the Hill group modified their own *β*-diketiminato magnesium hydride [HC{(Me)CNDipp}MgH] catalyst via hydride abstraction with $HB(C_6F_5)_3$.[140] The resulting magnesium compound $[HC\{(Me)CNDipp\}_2Mg(HB(C_6F_5)_3)$ has been applied in the catalytic hydroboration of N,N′-diisopropyl carbodiimide with HBpin. The product, bis(N-boryl)aminal $H_2C(N\{Bpin\}^iPr)_2$ was obtained in > 90% conversion at room temperature in 30 h or within 6 h at 60 °C.[140]

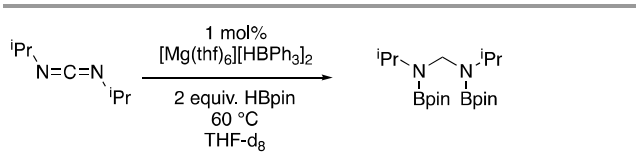
Virtually simultaneously, the Parkin group described the synthesis of a terminal magnesium hydride compound with tris[(1-isopropylbenzimidazol-2-yl)-dimethylsilyl)]methyl ligand, $[Tism^{PriBenz}]MgH$.[141] This complex features a carbatrane motif provided by the tris-[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl ligand (**Figure 12 c**). Significantly, [TismPriBenz]MgH is an effective catalyst at room temperature. Hydroboration of N,N′-Dicyclohexycarbodiimide and N,N′-Diisopropylcarbodiimide is carried out under 10 mol % of this catalyst in a J. Young NMR tube. 1.5 eq. HBpin is used in C_6D_6 as solvent in the presence of mesitylene as internal standard. The reaction is monitored by ^1H NMR. Substrate consumption was complete in 1 hour and TOFs of 6.5 and 8.5 h^{-1} were obtained respectively.[141]

In the same year, a magnesium hydridotriphenylborate $[Mg(thf)_6][HBPh_3]_2$ complex was synthesized as a solvent-separated ion pair (SSIP) as colorless crystals (**Scheme 44**). In this report, one example of carbodiimide hydroboration was disclosed employing this catalyst.[142] Dihydroboration of N,N-diisopropyl carbodiimide was achieved under 1 mol % catalyst loading at 60°C within 12h (**Scheme 45**).[142]

The first Al catalyst successfully deployed in carbodiimide hydroboration was reported in 2019.[82] Here, a β-diketiminato bis-n-butylaluminum of $LAl(n\text{-}Bu)_2$ (L = $(ArNCMe)_2CH$, Ar = 2,6-$^iPr_2C_6H_4$) was found to be effective in single hydroboration of carbodiimides. Hydroboration of N,N′-Diisopropylcarbodiimide in the presence of 3 mol % Al catalyst under neat conditions at 60 °C resulted in 99% yield. Furthermore, bis(tert-butyl)carbodiimide, bis-(cyclohexyl)carbodiimide, and bis(2,6- diisopropylphenyl)-carbodiimide were reduced to the corresponding singly hydroborated N-borylformamidine [RNCHN(BPin)R] in excellent yields (**Scheme 46**).[82]



Scheme 44. Synthesis of $[Mg(thf)_6][HBPh_3]_2$ catalyst via β-SiH abstraction.[142]

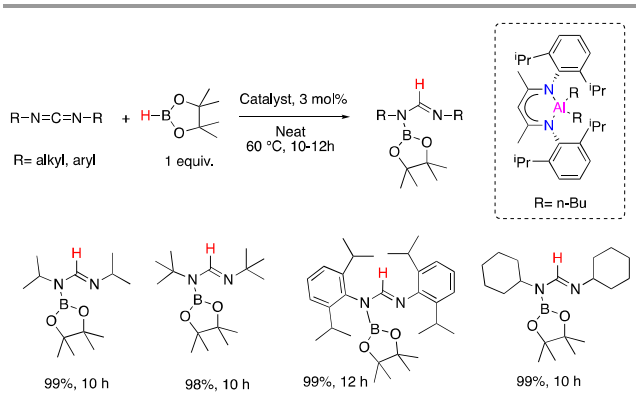


Scheme 45. Catalytic dihydroboration of N,N′-diisopropyl carbodiimide.[142]

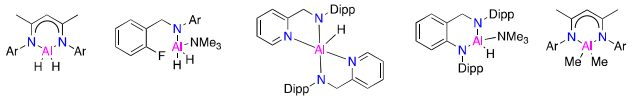
Roesky, Ma and Yang synthesized organoaluminum complexes (**Scheme 47**) which allow access to mononhydroboration of commercially available carbodiimides in the presence of 1.1 eq.

HBpin, 4 mol % catalyst under neat condition at 80 °C.[81] Various aluminum hydride and aluminum alkyls were synthesized and investigated as potential catalysts in these transformations. Hydroborated products using four different aluminum complexes (4 mol %) under neat condition are summarized in **Table 8** and **9**.[81] Surprisingly, the formation of monohydroborated C-borylformamidine product was also observed (**Scheme 48**) with the extension of heating time. This product has not been observed under previous reports. The reaction was proposed to procced through an aluminum formamidinate compound, which is depicted in **Scheme 49**.[81]

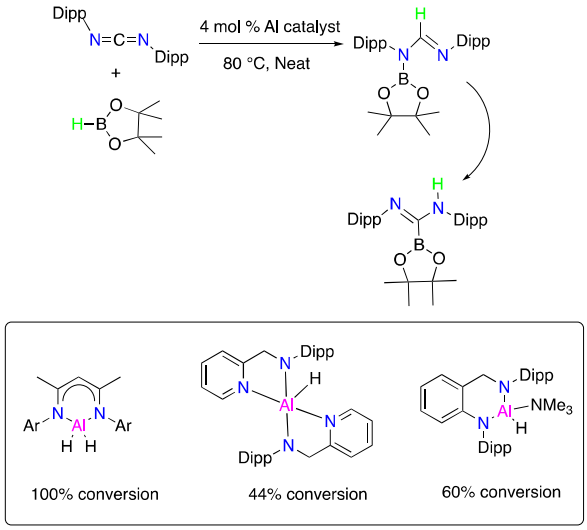
In 2019, 9-borabicyclo[3.3.1]nonane dimer was reported as a metal-free catalyst in carbodiimide hydroboration with pinacolborane.[143] $(H\text{-}BBN)_2$ is usually applied as a hydroboration agent and is rarely used as a catalyst. However, this report detailed that in some cases it can be a highly active catalyst (more so than some reported metal-based catalysts).[143] A broad substrate scope was studied using this catalyst; including aliphatic, aromatic, sterically encumbered and asymmetric substrates. Excellent conversion of 99% was obtained in most of the substrates under low catalyst loading of 0.5-2 mol % at 25-60 °C.



Scheme 46. Single hydroboration of carbodiimide in the presence of $LAl(n\text{-}Bu)_2$ as catalyst.[82]



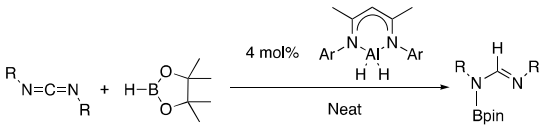
Scheme 47. Organoalminium complexes in carbodiimide hydroboration (Ar= 2,6-$Et_2C_6H_3$, Dipp).[81]



Scheme 48. Hydroboration of carbodiimide in the presence of different Al complexes.[81]

The highest activity (> 99% conversion) was observed in hydroboration of N,N′-Dicyclohexycarbodiimide using 0.5 mol % catalyst in 2 h at 25 °C. The lowest conversion of 23% was observed for the substrate with $SiMe_3$ group ($SiMe_3N{=}C{=}NSiMe_3$). The reaction times varied widely 0.2-90 h (**Table 10**).

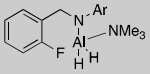
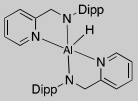
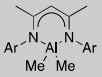
Table 8. Optimization for the monohydroboration of different carbodiimides using aluminum complex as the catalyst.[81]



Entry[a]	RNCNR	t (h)	T (°C)	Yield[b](%)
1	^{i}Pr	12	70	79
2			80	96
3	Cy	12	70	81
4			80	97
5	^{t}Bu	60	70	34
6			80	69
7	2,6-^{i}Pr$_2$C$_6$H$_3$	4	70	96
8		2	80	99

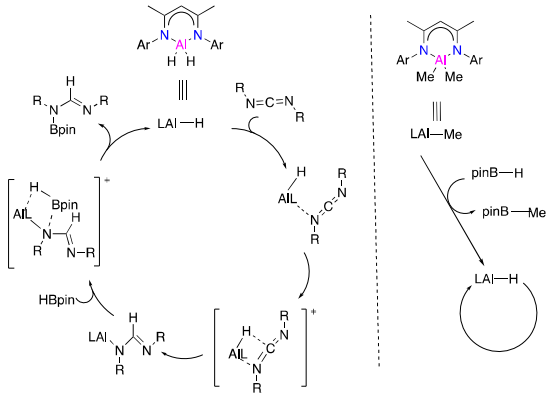
Reaction conditions: 0.04 mmol catalyst, 1.1 mmol HBpin, 1 mmol carbodiimide. [b] ^{1}H NMR analysis.

Table 9. Catalytic monohydroboration of different carbodiimides using aluminum complexes as a precatalyst.[81]

Entry[a]	Catalyst	RNCNR	t(h)	Yield (%)[b]
1		^{i}Pr	24	99
2		Cy	24	95
3		^{t}Bu	40	96
4		2,6-^{i}Pr$_2$C$_6$H$_3$	48	95
5		^{i}Pr	24	98
6		Cy	24	99
7		^{t}Bu	60	31
8		2,6-^{i}Pr$_2$C$_6$H$_3$	36	44
9		^{i}Pr	24	93
10		Cy	24	91
11		^{t}Bu	40	73
12		2,6-^{i}Pr$_2$C$_6$H$_3$	48	77

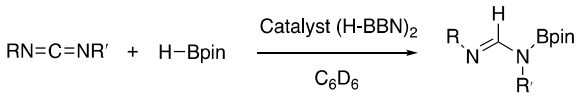
[a]Reaction conditions: 0.04 mmol catalyst, 1.1 mmol HBpin, 1 mmol carbodiimide, at 80 °C. [b]By 1H NMR analysis.

Stoichiometric reactions and kinetic analysis were performed to better understand the mechanism of the reaction. The boron amidinates $CH(NiPr)_2BBN$ and $CH(NDipp)_2BBN$ were prepared through the direct reaction of the corresponding carbodiimide and $(H\text{-}BBN)_2$. Stoichiometric reactions with equimolar amounts of HBpin and boron-amidinate were carried out at room temperature as depicted in **Scheme 50**. Formamidinato-H-BBN adduct was not observed in the presence of $CH(NDipp)_2BBN$ which might be less energetically favored due to bulky Dipp groups.[143]



Scheme 49. Suggested mechanism for the hydroboration of carbodiimides catalyzed by aluminum hydride and aluminum methyl complexes.[81]

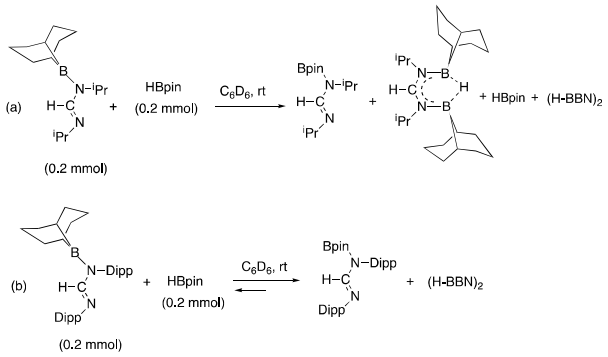
Table 10. Monohydroboration of carbodiimides using 9-BBN.[143]



Entry[a]	R, R′	Catalyst loading	t (h)	T (°C)	Conv. (%)[b]
1	^{i}Pr	2.5	0.2	25	>99
2	^{i}Pr	0.5	2	25	>99
3	Cy	2.5	0.2	25	>99
4	Cy	0.5	2	25	>99
5	^{t}Bu	2.5	3.5	25	>99
6	^{t}Bu	0.5	2.5	60	99
7	*p*-Tol	2.5	1	60	>99
8	*p*-Tol	0.5	2.5	60	>99
9	Dipp	2.5	2.5	25	>99
10	Dipp	0.5	2.5	60	>99
11	$SiMe_3$	2.5	3.5	60	23
12	Et, ^{t}Bu	2.5	20	60	>99
13	Et, ^{t}Bu	0.5	90	60	93
14	Et,$(CH_2)_3NMe_2$[c]	2.5	15	60	>99
15	Et,$(CH_2)_3NMe_2$[c]	0.5	20	60	>99

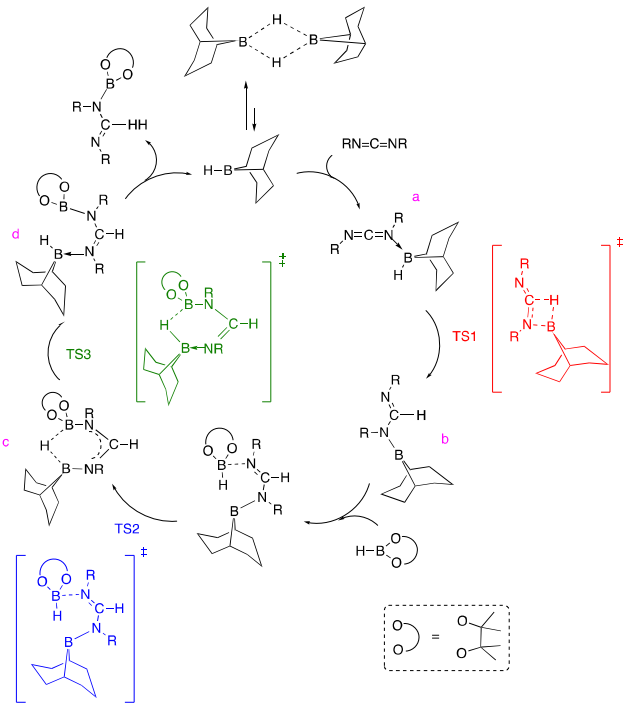
[a]Reaction condition: (RNCNR′, 0.20 mmol), HBpin (0.20 mmol) $(H\text{-}BBN)_2$ as a catalyst in benzene. [b]Determined by ^{1}H NMR spectroscopy. [c]Isomer mixture 43:57.

The experimental studies were supported by DFT calculations and resulted in the proposed mechanism depicted in **Scheme 51** which involves the formation of an adduct between carbodiimide and H-BBN (**a** in **Scheme 51**). Followed by the corresponding formamidinate complex (**b** in **Scheme 51**). The formamidinate compounds can form adducts with HBpin and rearrange to the energetically more stable heterocyclic intermediate (**c** in **Scheme 51**). The hydride transfer to BBN leads to the formation of adduct **d**. Finally, release of the H-BBN molecule, and rotation about the C–N single bond, affords the final product.[143]

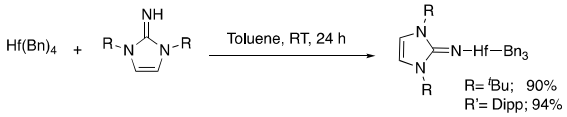


Scheme 50. Stoichiometric reactions between a) $CH(N\textit{i}Pr)_2BBN$ and HBpin, b) $CH(NDipp)_2BBN$ and HBpin.[143]

In 2020, an unprecedented organometallic hafnium hydride complex was introduced by the Eisen group. This Lewis acid catalyst is effective in carbodiimide hydroboration. This complex was prepared via the proteolysis of hafnium tetrabenzyl and N-heterocyclic imidazolin-2-imine ligands (**Scheme 52**).



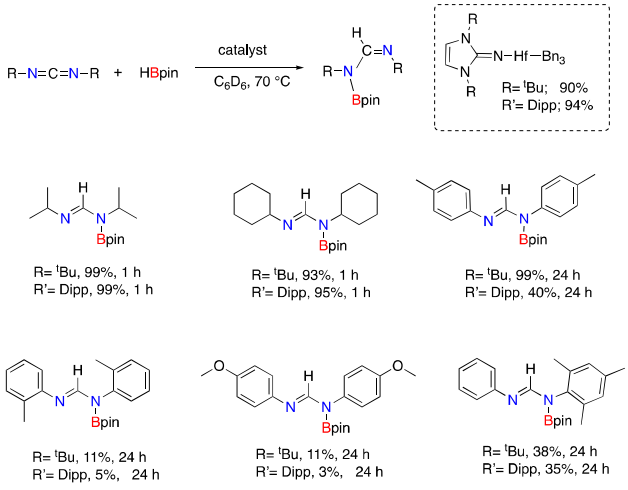
Scheme 51. Proposed catalytic cycle for the monohydroboration of carbodiimides catalyzed by $(H\text{-}BBN)_2$.[143]



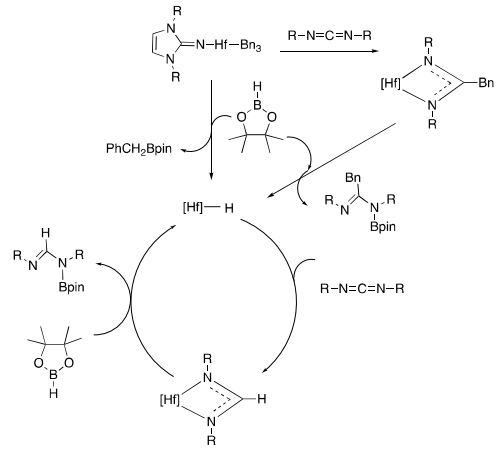
Scheme 52. Synthesis of mono(imidazoline-2-iminato) hafnium (IV) complexes.[144]

The electronic properties of these ancillary ligands decrease the oxophilicity of the metal center along with their steric demand which prevents possibility of the formation of bridging Hf-O-Hf macrocyclic complexes. Highly selective product formation (monoborylation) was achieved even with excess amounts of HBpin. Catalytic reactions proceed with singly reduced amidinate product formed within one hour for aliphatic carbodiimides. However, longer reaction times were required for aromatic carbodiimides. The hydroboration reaction was inhibited by the presence of electron donating substituents at the backbone of aromatic carbodiimides (**Scheme 53**). Based upon an examination of stoichiometric reactions it is proposed that the first step of the catalytic process is σ-bond metathesis between the hafnium complex and HBpin to form a Hf-H species. Subsequently, carbodiimide insertion takes place into the Hf-H bond which produces the hafnium amidinate complex (**Scheme 54**).[144]

Later in 2021, Von Wangelin group reported a Mn(II) pre-catalyst supported by hmds ligands ($Mn(hmds)_2$) in the hydroboration of a wide array of functional groups including carbodiimides.[131] $Mn(hmds)_2$ (5 mol %) is used in the presence of 1.1 eq HBpin at 20-80 °C for the selective monoreduction of carbodiimides within 20 h (78-95%).



Scheme 53. Monohydroboration of carbodiimides using Hf complexes.[144] Reaction conditions: 0.155 mmol of carbodiimide, 0.155 mmol of HBpin, and 0.0015 mmol of catalyst in 600 µL of C_6D_6 at 70 °C. The reactions are monitored by ^1H NMR.



Scheme 54. Plausible mechanism for the catalytic hydroboration of carbodiimide.[144]

Bulky carbodiimides with ^{t}Bu and Dipp groups were cleanly converted to products, 78 % and 83% yield respectively but required elevated reaction temperature. It was noteworthy, that no double reduction products were observed even in the presence of excess amounts of HBpin. Regioselective hydroboration was observed with unsymmetrical carbodiimide (N-tert-butyl-N'-ethylcarbodiimide) which is exclusively converted to the ethylaminoboronate isomer in 92 % yield.[131]

In the same year of 2021, Ma and Yang reported *n*-BuLi as catalyst in monohydroboration of carbodiimides under neat condition at 80 °C. Both aliphatic and aromatic carbodiimides (3 examples) underwent reduction with yield of 97-99% within 24-48 h.[137]

Sen group reported lithium complexes, 2,6-di-tert-butyl phenolate lithium and 1,1'- dilithioferrocene (**Figure 12k**) in carbodiimide hydroboration in 2021. 4 examples studied using 4 mol % catalyst loading, neat condition at 80 °C with 1H NMR yield of 30-99%.[145]

5. Conclusions and outlook

In summary, we have reviewed the recent developments in the catalytic hydroboration of imines, nitriles, and carbodiimides. Both steric and electronic features of these molecules tend to make their interactions with catalysts less favorable compared to aldehydes and ketones. In particular, the steric constraints make hydroboration challenging in nitrile substrates. HBpin, HBcat and 9-BBN have been deployed as borylating agent in most catalytic applications; within this subset of boranes reports employing HBpin are dominant, which is attributed to its Lewis acidity and relative stability which reduces the difficulty in handling other boranes which exhibit air- and moisture-instability. These hydroboration transformations underwent mainly through: Oxidative addition of B-H bond[6, 92, 124], strong base-induced nucleophilic attack[105], radical pathway[46, 120] or sigma-bond metathesis[144].

Imine substrates were studied with a wide array of catalysts ranging from main group elements to transition metals. The highest reported TOF of 400 h^{-1} was achieved employing zinc dihydrides catalyst with N-heterocyclic carbene ligands in the aldimine hydroboration. In contrast, amongst reported main group element catalysts, the β-diketiminato magnesium alkyl [LMg^{n}Bu] (L = CH[CMe(NDipp)]$_2$) complex afforded the highest TOF (99 h^{-1}). Most transition metal systems share common mechanistic details and, at some stage of the reaction the formation of a metal hydride species is implied. These pathways are typically supported by either experimental or computational studies. It is important to note that the underlying mechanisms of paramagnetic catalysts require further study. Despite impressive advances in the field, there are still challenges which need to be overcome: (1) There is an ongoing need to extend and develop current base metal catalysts. Clearly, ligand design principles related to non-innocence are of interest in emulating the efficacy of precious metal catalysis. (2) The use of ketimine substrates is underdeveloped compared to aldimines, often ketimines are sluggish or simply do not react under mild reaction conditions. (3) Currently, there remains only a handful of examples of chemoselective hydroboration in the presence of a large number of functional groups such as carbonyl and alkene have remained elusive. (4) Asymmetric hydroboration of imines need to be further studied.

Nitrile hydroboration has steadily gained attention in the last decade. There are many reports utilizing both transition metals and main group elements as catalysts.[67, 71, 122, 134] Ru and Co catalysts are more studied among precious metals and base metal elements, respectively.[47, 73, 75] Metallacyclic thorium amide complex ([(Me$_3$Si)$_2$N]$_2$Th[κ^2–(N,C)–CH$_2$Si(CH$_3$)$_2$N(SiMe$_3$)] gained one of the highest TOFs (500 h^{-1}) among transition metal catalysts.[49] Main group element catalysts in nitrile hydroboration are mainly dominated by Al complexes.[82, 133 31, 135] However, sodium triethylborohydride (NaHBEt$_3$) gained one the highest TOFs (2400 h^{-1}) among main group catalysts.[69] Along with the promising developments in nitrile hydroboration there remain several important challenges as follows: (1) there are few examples of rare earth metal catalysts. (2) selectively accessing singly hydroborylated products is difficult, as most reports focus on double hydroboration of nitriles. (3) Chemoselectivity in the presence of reducible functional groups, such as NO_2, carbonyl, alkene, ester etc. are limited and most reports exhibit limited tolerance (halogens, electron donating groups, and heteroatoms etc.). Future work is expected to focus more on designing catalysts based upon rare earth metals and employ the catalysis in both mono and dihydroboration with improvement in chemoselectivity.

Carbodiimide reduction is not very well studied, and Mg catalysts mostly dominate the field. 9-BBN which is usually reported as hydroboration reagent has been shown to act as a catalyst in carbodiimide monohydroboration. However, mono(imidazolin-2-iminato) Hafnium complex revealed to have the highest TOF (102 h^1) among the other catalysts in carbodiimide hydroboration.[144] There are still challenges associated with hydroboration of these nitrogenous compounds: (1) There are only handful reports of catalysts exist which are mainly based on main group elements. (2) Substrate scope is very limited. (3) Dihydroboration of carbodiimide has not been investigated. Therefore, there are still opportunities to develop catalysts based on transition metals to achieve both mono and dihydroboration along with chemoselective studies.

Author Contributions

Conflicts of interest

There are no conflicts to declare.

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